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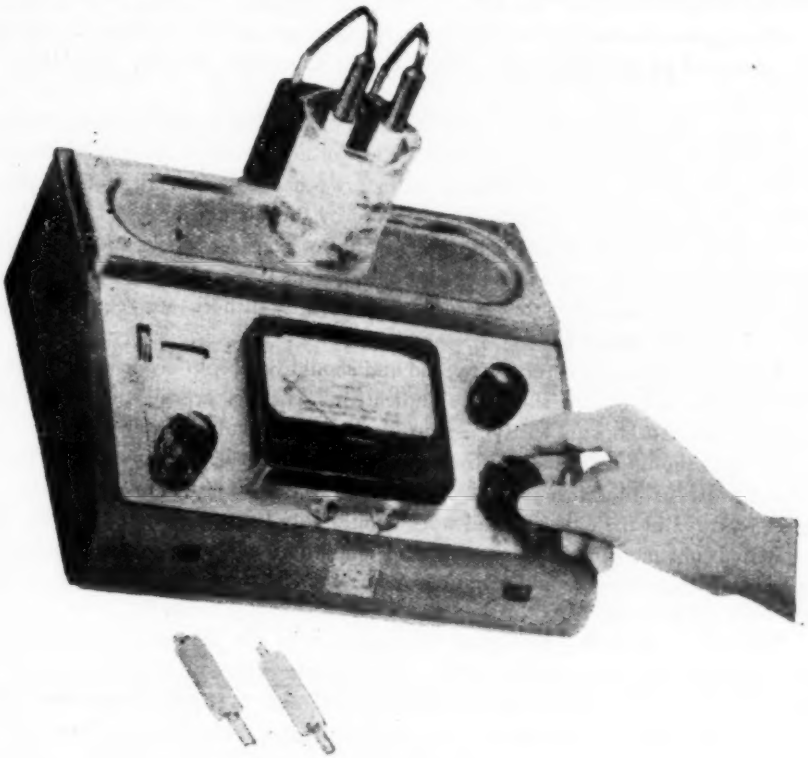

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[Jour. Indian Chem. Soc., Vol. 35, No. 4, 1958]

STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION. PART XLIX. THE ROTATORY DISPERSION OF *o*-, *m*-, *p*-METHOXY- AND ETHOXY-PHENYLIMINO-*d*-CAMPHORS AND *p*-SULPHONAMIDO-, *o*- AND *p*-METHOXYPHENYLAMINO-*d*-CAMPHORS

By Bawa Kartar Singh and Bhupendra Sahai Saxena

The rotatory dispersion of *o*-, *m*-, *p*-methoxy- and ethoxy-phenylimino-*d*-camphors and *p*-sulphonamido-, *o*- and *p*-methoxyphenylamino-*d*-camphors has been studied in seven solvents. It is found to be '*simple*' as it can be expressed by 'one-term' Drude's equation. The values of the 'characteristic' wave-lengths (λ_0s) vary from about 3510 Å to 4240 Å for the arylimino compounds, whereas they are considerably less, being about 1850 to 3100 Å for the corresponding arylamino compounds.

The effect of position isomerism and the influence of solvents on rotatory power have been studied. The significant effect of conjugated double bonds on rotatory power has also been discussed.

In the present investigation, we have determined the rotatory power of *o*-, *m*-, *p*-methoxy- and ethoxy-phenylimino-*d*-camphors and *p*-sulphonamido-, *o*- and *p*-methoxyphenylamino-*d*-camphors in seven solvents.

Whereas the rotatory dispersion of the colorless arylamino compounds has been recorded for thirteen wave-lengths (6708 to 4358Å) in the visible region of the spectrum, it is given for only eight lines (6708 to 5209Å) in the case of coloured arylimino compounds.

Nature of the Rotatory Dispersion

The compounds described here exhibit '*simple*' rotatory dispersion in all the solvents as their rotatory power can be expressed by Drude's *one-term* equation,

$$[\alpha]_\lambda = \frac{K}{\lambda^2 - \lambda_0^2}$$

where 'K' is the rotation constant and λ_0^2, the dispersion constant.

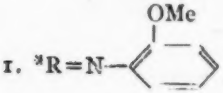
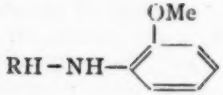
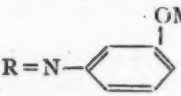
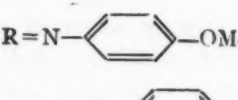
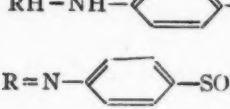
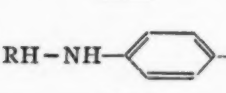
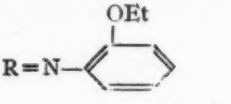
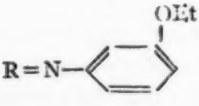
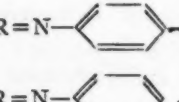
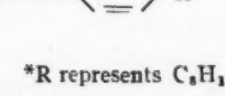
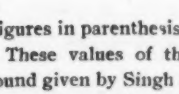
The values of λ_0s, the 'characteristic' wave-lengths, vary from 3513 to 4239Å for the yellow-coloured arylimino compounds, whereas those for the colorless arylamino compounds are considerably less, being 1847 to 3095Å, showing that the rotations of these arylamino compounds are controlled by the low-frequency characteristic of the 'keto' group, pertaining to the selective absorption band (λ_{max} 2880) of camphor (Lowry and French, *J. Chem. Soc.*, 1924, **125**, 1923) and sometimes by the high frequency corresponding to the general absorption of the saturated molecules (indicated by italicized figure of values of λ_0s in Tables V, VI and VII).

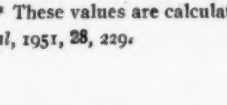
While the absorption maxima (λ_{max}) of the arylamino compounds (this *issue*, p. 227) substantially support the 'characteristic' wave-lengths (λ_0s), derived from Drude's equation, the high values of the λ_0s of the arylimino compounds, specially λ_0 = 4000 Å to λ_0 = 4239 Å, do not support the absorption spectra data which give two λ_{max} at about 270 and 350 mμ for these compounds.

An explanation of this discrepancy will be given under the ultraviolet absorption spectra of these compounds.

TABLE A

lecular rotatory power $[M]^{35}_{5461}$ in different solvents.

Compounds.	MeOH. (31.1)	EtOH. (25.8)	Acetone. (21.5)	Pyridine. (12.4)	EtOAc. (6.11)	$CHCl_3$. (5.2)	Benzene. (2.28)
1. *R=N– 	672.08	674.79	661.24	742.54	639.56	750.67	712.73
2. RH–NH– 	226.59	241.61	274.37	214.31	288.02	324.87	248.43
3. R=N– 	1940.4	1986.4	1924.1	2238.5	2010.8	2127.4	2241.2
4. R=N– 	3902.4	4092.0	3891.6	4373.9	3945.8	4363.0	4390.2
5. RH–NH– 	230.69	245.70	256.62	144.69	285.29	309.86	296.21
6. R=N–  †	1445.8	1559.4	1628.8	1646.7	...	1710.4	...
7. RH–NH– 	301.07	304.29	299.46	170.66	354.2	389.62	...
8. R=N– 	612.75	621.30	652.65	715.35	661.20	703.95	745.7
9. R=N– 	1952.3	1963.7	2017.8	2109.0	2034.9	2054.8	2114.7
10. R=N– 	4172.4	4195.2	4106.9	4639.8	4126.8	4611.3	4619.9
11. R=N–  **	1929.9	2032.4	1966.1	2193.8	...	2130.3	2234.6

*R represents 

Figures in parenthesis indicate the dielectric constants of pure solvents.

† These values of the molecular rotation are calculated from the specific rotation values of this compound given by Singh and Manhas, *Proc. Ind. Acad. Sci.*, 1949, **30A**, 87.

** These values are calculated from the specific rotation of this compound by Singh and Singh, this *Journal*, 1951, **28**, 229.

Position Isomerism and Rotatory Power

The rotatory powers of methoxyphenylimino- and ethoxyphenylimino *d*-camphors do not obey Cohen's rule (*J. Chem. Soc.*, 1910, **97**, 1739). The order of the rotatory power, $[\alpha]^{35}_{5461}$, of these compounds in different solvents is $o < m < un < p$. These compounds therefore also do not obey Frankland's *'lever-arm'* hypothesis (*ibid.*, 1896, **69**, 1309).

The rotatory powers of the methoxy compounds are found to be always higher than those of the corresponding ethoxy compounds. Some departure from this generalisation is, however, to be noted in the *para* isomers where the rotatory power of the ethoxy compound exceeds that of the methoxy derivative for shorter wave-lengths in some of the solvents (Tables III, IV and X).

Influence of Solvents on Rotatory Power

With the exception of the behaviour of acetone and pyridine in several cases, it is found that generally the rotatory power increases as the dielectric constant of the solvents decreases (Table A).

Effect of Conjugated Double Bonds on Rotatory Power

A stuudy of Table A reveals that there is a big fall in the values of molecular rotatory power, $[M]^{35}_{5461}$, as we pass from the arylimino- to the corresponding arylamino-*d*-camphors. This remarkable depression in the molecular rotatory power must be correlated with the reduction of the imino group $>C=N-$ to the amino group $>CH-NH-$, *i.e.*, with the break in the conjugation of the double bonds of the carbonyl- azethenoid phenyl groups of the arylimino compounds at the dotted line:

$[M]^{35}_{5461} = 4374°$ (Pyridine) $\longrightarrow$ $[M]^{35}_{5461} = 145°$ (Pyridine)

The depression in the rotatory power is remarkable in the case of the *p*-methoxyphenylimino-*d*-camphor (Table A).

This depression in the molecular rotatory power is also accompanied by a marked decrease in the value of the 'characteristic' wave-length from a range of 3513-4239 Å to 1847–3095 Å (Tables I to VII).

TABLE I

o-*Methoxyphenylimino*-d-*camphor* (m.p. 120°).

Solvents:	MeOH (31.5)*		EtOH (25.8)		Acetone (21.5)		Pyridine (12.4)		Et acetate (6.11)		$CHCl_3$ (5.2)		Benzene (2.28)	
Conc. (g./100 c.c.):	0.5000		0.5000		0.5000		0.2500		0.2500		0.5000		0.5000	
Calc. $[\alpha]_{\lambda}^{35}$ =	$\frac{42.065}{\lambda^2-0.1289}$		$\frac{39.988}{\lambda^2-0.1376}$		$\frac{38.963}{\lambda^2-0.1383}$		$\frac{42.20}{\lambda^2-0.1442}$		$\frac{39.67}{\lambda^2-0.1301}$		$\frac{45.649}{\lambda^2-0.133}$		$\frac{45.723}{\lambda^2-0.1234}$	
λ_0(Å) =	3591		3710		3720		3798		3607		3647		3513	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	131.0	131.00	128.0	128.00	125.0	125.00	138.0	137.99	124.0	124.00	144.0	144.00	140.0	139.99
6438	148.0	147.28	144.0	144.41	140.0	141.06	156.0	156.12	140.0	139.48	162.0	162.16	156.0	157.07
6104	172.0	172.68	170.0	170.23	166.0	166.36	184.0	184.84	164.0	163.65	190.0	190.60	184.0	183.55
5893	193.0	192.69	191.0	190.78	186.0	186.51	208.0	207.88	182.0	182.72	216.0	213.11	204.0	204.30
5780	205.0	204.99	204.0	203.50	199.0	198.99	222.0	222.22	196.0	194.46	227.0	226.99	217.0	217.00
5468	247.0	247.29	247.0	247.75	243.0	242.45	274.0	272.60	234.0	234.87	274.0	274.99	261.0	260.38
5461	248.0	248.46	249.0	248.99	244.0	243.67	274.0	274.10	236.0	235.99	277.0	276.32	263.0	261.57
5209	296.0	295.40	300.0	299.08	291.0	292.95	...	...	282.0	280.94	...	...	...	...

* Figures in parentheses are the values of the dielectric constants of the solvents.

TABLE II

m-*Methoxyphenylimino*-d-*camphor* (m.p. 78 5°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.):	0.5000		0.5000		0.5000		0.5000		0.5000		0.5000		0.5000	
Calc. $[\alpha]_{\lambda}^{35} =$	$\frac{99.95}{\lambda^2-0.1586}$		$\frac{102.8}{\lambda^2-0.1579}$		$\frac{100.74}{\lambda^2-0.1563}$		$\frac{108.94}{\lambda^2-0.1663}$		$\frac{101.13}{\lambda^2-0.1619}$		$\frac{108.96}{\lambda^2-0.1594}$		$\frac{109.18}{\lambda^2-0.1664}$	
λ_0(Å) =	3683		3975		3953		4078		4024		3993		4079	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	343.0	343.00	352.0	351.99	343.0	343.00	384.0	383.99	351.0	351.02	375.0	374.95	385.0	384.97
6438	391.0	390.58	400.0	400.64	389.0	390.16	440.0	438.92	401.0	400.35	428.0	427.12	441.0	440.06
6104	468.0	467.27	478.0	479.05	465.0	465.95	527.0	528.32	480.0	480.19	510.0	511.30	529.0	529.74
5893	529.0	529.95	545.0	543.11	529.0	527.71	601.0	602.21	545.0	545.76	581.0	580.19	605.0	603.87
5780	571.0	569.51	585.0	583.59	567.0	566.59	650.0	649.22	589.0	587.28	625.0	623.69	651.0	651.64
5468	711.0	711.89	728.0	728.87	705.0	705.95	821.0	820.94	737.0	737.63	780.0	780.51	824.0	823.37
5461	716.0	715.97	733.0	732.97	710.0	709.93	826.0	825.92	742.0	741.97	785.0	785.01	827.0	828.37
5209	885.0	886.86	908.0	906.61	876.0	876.00	...	...	923.0	924.40	972.0	973.72	1039.0	1040.8

TABLE III

p-*Methoxyphenylimino*-d-*camphor* (α-*form*, m.p. 114.5°).

Solvents:		MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.):		0.5000		0.5000		0.5000		0.2500		0.2500		0.2500		0.2500	
Calc.	$[\alpha]_{\lambda}^{35} =$	$\frac{188.63}{\lambda^2-0.1672}$		$\frac{195.99}{\lambda^2-0.1684}$		$\frac{185.99}{\lambda^2-0.1686}$		$\frac{199.32}{\lambda^2-0.1747}$		$\frac{189.43}{\lambda^2-0.1681}$		$\frac{199.66}{\lambda^2-0.1742}$		$\frac{196.57}{\lambda^2-0.1770}$	
	λ_0(Å) =	4088		4104		4107		4180		4100		4174		4208	
Lines.		*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708		667.0	667.0	696.0	696.0	661.0	661.0	724.0	724.1	672.0	672.0	724.0	723.9	720.0	720.0
6438		763.0	762.7	795.0	796.0	755.0	756.4	832.0	831.2	768.0	768.8	828.0	830.9	826.0	827.7
6104		916.0	918.8	958.0	960.3	912.0	912.2	1008.0	1007.7	926.0	926.8	1026.0	1006.9	1006.0	1005.4
5893		1046.0	1047.9	1098.0	1096.1	1040.0	1041.3	1154.0	1155.5	1058.0	1057.7	1156.0	1154.1	1156.0	1154.9
5780		1130.0	1130.1	1184.0	1182.8	1124.0	1123.8	1250.0	1250.4	1140.0	1141.1	1248.0	1248.7	1250.0	1251.2
5468		1433.0	1431.1	1501.0	1500.6	1424.0	1426.3	1606.0	1603.5	1444.0	1447.1	1598.0	1599.8	1614.0	1611.2
5461		1440.0	1439.9	1510.0	1510.0	1435.0	1435.0	1614.0	1614.0	1456.0	1456.0	1610.0	1610.1	1622.0	1621.9
5200		1814.0	1812.0	1902.0	1904.7	1810.0	1811.0	2060.0	2063.4	1832.0	1836.0	2054.0	2056.2	2080.0	2084.5

TABLE IV

p-*Methoxyphenylimino*-d-*camphor* (*β-form*, m.p. 120°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.):	0.2500		0.2500		0.2500		0.2500		0.2500		0.2500		0.2500	
Calc. $[\alpha]_{\lambda}^{35} =$	$\frac{188.92}{\lambda^2-0.1672}$		$\frac{195.99}{\lambda^2-0.1684}$		$\frac{186.45}{\lambda^2-0.1684}$		$\frac{199.32}{\lambda^2-0.1747}$		$\frac{189.43}{\lambda^2-0.1681}$		$\frac{199.66}{\lambda^2-0.1742}$		$\frac{196.73}{\lambda^2-0.1768}$	
λ_0 (Å) =	4088		4104		4104		4180		4100		4174		4206	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	668.0	668.0	696.0	695.0	662.0	662.1	724.0	724.1	672.0	672.0	724.0	723.9	720.0	720.1
6438	762.0	763.9	794.0	796.3	754.0	757.6	830.0	831.2	770.0	768.8	828.0	830.9	824.0	827.7
6104	920.0	920.2	956.0	960.3	916.0	913.5	1004.0	1007.7	928.0	926.8	1008.0	1006.9	1002.0	1005.3
5893	1054.0	1049.5	1100.0	1096.1	1048.0	1042.8	1156.0	1155.5	1054.0	1057.7	1154.0	1154.1	1154.0	1154.5
5780	1132.0	1132.0	1184.0	1182.8	1120.0	1125.2	1250.0	1250.4	1136.0	1141.1	1250.0	1248.7	1250.0	1250.7
5468	1438.0	1433.4	1506.0	1500.6	1426.0	1427.6	1606.0	1603.5	1444.0	1447.1	1600.0	1599.8	1612.0	1609.9
5461	1440.0	1442.1	1510.0	1510.0	1436.0	1436.0	1614.0	1614.0	1456.0	1456.0	1610.0	1610.1	1620.0	1620.0
5209	1816.0	1814.8	1900.0	1904.7	1816.0	1811.9	2060.0	2063.4	...	...	2054.0	2056.2	...	...

TABLE V

o-*Methoxyphenylamino*-d-*camphor* (m.p. 148°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		Chloroform		Benzene	
Conc. (g./100 c.c.):	1.0000		1.0000		1.0000		1.0000		1.0000		1.0000		1.0000	
Calc. $[\alpha]_{\lambda}^{35} =$	$\frac{21.132}{\lambda^2-0.0436}$		$\frac{21.532}{\lambda^2-0.0549}$		$\frac{24.571}{\lambda^2-0.0537}$		$\frac{18.259}{\lambda^2-0.0656}$		$\frac{24.34}{\lambda^2-0.0668}$		$\frac{25.81}{\lambda^2-0.0813}$		$\frac{20.157}{\lambda^2-0.0767}$	
$\lambda_0(\text{Å}) =$	2088		2343		2318		2562		2585		2851		2770	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	52.0	52.00	54.5	54.50	62.0	62.00	47.5	47.50	63.0	63.51	70.5	70.0	53.5	54.00
6438	57.5	56.97	60.5	59.87	68.0	68.10	52.5	52.33	70.0	70.00	78.0	77.45	60.0	59.67
6104	64.0	64.25	67.5	67.79	77.0	77.07	59.0	59.49	80.0	79.62	88.0	88.63	68.0	68.14
5893	70.5	69.60	74.0	73.66	84.0	83.72	64.5	64.84	86.5	86.80	97.5	97.07	74.5	74.50
5780	73.5	72.74	77.5	77.12	88.0	87.62	68.0	68.00	91.5	91.05	102.0	102.09	78.5	78.31
5468	82.5	81.74	88.0	88 21	100.0	100.16	78.5	78.23	104.5	104.82	118.0	118.55	90.5	90.67
5461	83.0	83.00	88.5	88.50	100.5	100.49	78.5	78.49	105.5	105.18	119.0	118.99	91.0	91.00
5209	93.0	92.81	99.5	99.50	113.5	112.91	88.0	88.76	119.0	119.02	136.5	135.84	103.5	103.58
5087	97.5	98.24	106.5	105.65	119.5	119.85	94.0	94.55	127.5	126.83	145.5	145.49	111.5	110.75
4800	113.5	113.12	122.5	122.69	139.0	139.05	...	...	148.0	148.77	172.0	173.10	130.5	131.14
4678	120.5	120.55	130.5	131.29	149.5	148.73	...	...	160.0	160.02	187.0	187.57	142.0	141.75
4603	124.0	125.63	136.0	137.23	155.5	155.41	...	...	168.5	167.86	199.0	197.77	149.0	149.20
4358	142.0	144.34	160.5	159 37	179.5	180.27	...	...	197.5	197.56	236.0	237.44	177.0	177.91

TABLE VI

p-*Methoxyphenylamino*-d-*camphor* (m.p. 101°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.):	1.0000		1.0000		1.0000		1.0000		1.0000		1.0000		1.0000	
Calc. $[\alpha]_{\lambda}^{35}$ =	$\frac{20.119}{\lambda^2-0.0601}$		$\frac{20.591}{\lambda^2-0.0694}$		$\frac{23.726}{\lambda^2-0.0458}$		$\frac{13.276}{\lambda^2-0.0477}$		$\frac{22.687}{\lambda^2-0.0811}$		$\frac{23.508}{\lambda^2-0.0916}$		$\frac{21.9604}{\lambda^2-0.0958}$	
λ_0(Å) =	2452		2635		2140		2184		2848		3026		3095	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	51.5	51.60	54.0	54.10	58.5	58.70	33.0	33.0	61.5	61.50	65.5	65.50	62.0	62.00
6438	57 0	56.76	59.5	59.66	64.5	64.35	36.0	36.19	68.5	68.05	73.0	72.67	69.0	68.91
6104	64.5	64.40	68.0	67.93	72.0	72.62	41.0	40.87	77.5	77.86	83.5	83.52	79.0	79.37
5893	70.0	70.08	74.5	74.12	79.5	78.72	44.5	44.32	85.0	85.25	91.5	91.76	88.0	87.35
5780	73.0	73.43	78.0	77.79	83.0	82.29	46.0	46.35	90.5	89.67	97 0	96.72	92.5	92.15
5468	84.5	84.22	89.5	89.68	93.5	93.70	52.5	52.83	104.0	104.12	113.0	113.06	108.0	108.07
5461	84.5	84.50	90.0	89.99	94.0	94.00	53.0	52.99	104.5	104.50	113.5	113.50	108.5	108.50
5209	95.5	95.26	102.0	101.98	105.0	105.22	59.0	59.37	120.0	119.27	130.5	130.39	125.5	125.13
5087	100.5	101.30	109.0	108.77	112.0	111.44	63.5	62.92	128.0	127.74	140.0	140.27	134.0	134.81
4800	117.5	118.14	127.5	127.89	128.5	128.52	73.0	72.66	152.0	151.95	169.5	168.72	163.0	163.15
4678	127.5	126.69	138.0	137.73	136.5	137.06	...	...	164.0	164.63	183.3	183.95	179.0	178.39
4603	133.0	132.62	145.0	144.59	143.0	142.92	...	...	182.0	181.23	195.0	194.65	188.0	189.31
4358	155.0	154.98	170.0	170.73	164.5	164.53	...	...	208.0	208.32	237.0	237.71	234.0	233.12

TABLE VII

p-*Sulphonamidophenylamino*-d-*camphor* (m.p. 181.5°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$	
Conc. (g./100 c.c.):	1.0000		1.0000		0.5000		1.0000		0.5000		0.5000	
Calc. $[\alpha]_{\lambda}^{35} =$	$\frac{24.70}{\lambda^2-0.0341}$		$\frac{24.164}{\lambda^2-0.0425}$		$\frac{22.661}{\lambda^2-0.0533}$		$\frac{13.276}{\lambda^2-0.0477}$		$\frac{25.261}{\lambda^2-0.0686}$		$\frac{26.58}{\lambda^2-0.0783}$	
λ_0 (Å) =	1847		2062		2310		2184		2618		2798	
Lines.	o.	c.	o.	c.	o.	c.	o.	c.	o.	c.	o.	c.
6708	60.0	59.39	59.0	59.30	58.0	57.13	33.0	33.00	65.0	66.22	72.0	71.50
6438	64.5	64.93	65.0	64.96	62.0	62.74	36.5	36.19	73.0	73.01	78.0	79.02
6104	73.0	73.00	73.0	73.22	71.0	70.99	41.0	40.87	83.0	83.09	90.0	90.34
5893	79.5	78.89	79.5	79.30	78.0	77.10	44.5	44.32	91.0	90.65	99.0	98.82
5780	82.0	82.33	83.0	82.86	80.0	80.71	46.0	46.35	95.0	95.13	104.0	104.00
5468	93.5	93.24	94.0	94.21	92.0	92.24	52.5	52.83	109.0	109.62	120.0	120.40
5461	93.5	93 53	94.5	94.50	93.0	92.54	53.0	52.99	110.0	110.00	121.0	120.9
5209	105.0	104.20	106.5	105.61	103.0	103.94	59.5	59.37	125.0	124.57	138.0	137.0
5087	110.0	109.97	112.0	111.76	110.0	110.36	63.0	62.92	133.0	132.88	147.0	147.3
4800	125.5	125.82	128.0	128.60	127.0	127.62	73.5	72.66	155.0	155.60	174.0	174.3
4678	134.0	133.65	137.0	136.99	137.0	136.91	...	...	168.0	168.07	190.0	189.1
4603	139.0	139.00	141.5	142.72	143.0	143.00	...	...	176.0	176.31	199.0	199.1
4348	159.0	158.43	165.0	163.82	165.0	165.81	...	...	208.0	208.00	238.0	238.0

TABLE VIII

o-*Ethoxyphenylimino*-d-*camphor* (m.p. 53°).

Solvents:	MeOH		EtOH		Acetone		Pyridine		Et acetate		CHC'_3		Benzene	
Conc. (g./100 c.c.):	0.5000		0.5000		0.5000		0.5000		0.5000		0.5000		0.5000	
Calc. $[\alpha]_{\lambda}^{35}$ =	$\frac{35.495}{\lambda^2-0.1331}$		$\frac{30.192}{\lambda^2-0.1597}$		$\frac{36.935}{\lambda^2-0.1370}$		$\frac{37.800}{\lambda^2-0.1476}$		$\frac{35.218}{\lambda^2-0.1464}$		$\frac{34.243}{\lambda^2-0.1598}$		$\frac{42.92}{\lambda^2-0.1344}$	
Calc. λ_o(Å) =	3648		3996		3702		3843		3826		3997		3666	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	112.0	112.00	104.0	104.00	118.0	118.00	125.0	125.00	116.0	116.00	119.0	118.00	136.0	136.00
6438	126.0	126.14	118.0	118.49	134.0	133.10	141.0	141.62	132.0	131.35	134.0	134.44	153.0	153.23
6104	148.0	148.26	142.0	141.88	157.0	156.83	169.0	168.12	156.0	155.76	161.0	160.99	180.0	180.26
5893	166.0	165.78	162.0	161.02	175.0	175.71	190.0	189.37	175.0	175.38	183.0	182.73	202.0	201.69
5780	177.0	176.59	172.0	173.11	187.0	187.39	202.0	202.68	188.0	187.62	197.0	196.46	215.0	214.92
5468	214.0	213.95	216.0	216.74	228.0	227.99	249.0	249.66	230.0	230.78	246.0	246.00	260.0	260.75
5461	215.0	214.99	218.0	217.99	229.0	229.13	251.0	250.99	232.0	232.00	247.0	247.42	262.0	262.02
5209	258.6	256.83	270.0	270.54	274.0	275 01	306.0	305.57	283.0	281.96	308.0	307.12	314.0	313.51
5087	281.0	282.60	306.0	304.96	...	...	340.0	340.23	311.0	313.60	346.0	346.24	346.0	345.29

TABLE IX

m-*Ethoxyphenylimino*-d-*camphor* (m.p. 82.5°).

Solvents :	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.) :	0.5000		0.5000		0.5000		0.5000		0.5000		0.5000		0.5000	
Calc. $[\alpha]_{\lambda}^{35}$ =	$\frac{96.655}{\lambda^2-0.1571}$		$\frac{96.12}{\lambda^2-0.1587}$		$\frac{96.506}{\lambda^2-0.1619}$		$\frac{103.59}{\lambda^2-0.1582}$		$\frac{99.665}{\lambda^2-0.1586}$		$\frac{102.01}{\lambda^2-0.1594}$		$\frac{106.17}{\lambda^2-0.1551}$	
λ_0 (Å) =	3964		3985		4024		3977		3983		3993		3938	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c*	*o.*	*c.*	*o.*	*c.*
6708	330.0	330.0	330.0	330.0	335.0	335.0	355.0	355.0	342.0	342.0	351.0	351.0	360.0	360.0
6438	375.0	375.5	376.0	375.8	382.0	382.1	404.0	404.2	389.0	389.5	401.0	399.9	409.0	409.3
6104	449.0	448.7	451.0	449.6	460.0	458.2	485.0	483.4	467.0	465.9	479.0	478.7	489.0	488.4
5893	509.0	508.4	510.0	509.9	521.0	520.8	550.0	548.1	528.0	528.4	545.0	543.2	554.0	552.7
5780	546.0	546.1	547.0	548.0	562.0	560.4	589.0	588.9	569.0	567.9	582.0	583.9	594.0	593.1
5468	679.0	681.1	683.0	685.1	704.0	703.9	734.0	735.7	709.0	709.9	731.0	730.7	737.0	737.8
5461	685.0	685.0	689.0	689.0	708.0	708.0	740.0	739.9	714.0	713.9	735.0	734.9	742.0	741.9
5209	845.0	846.4	855.0	853.6	881.0	882.1	912.0	915.9	882.0	884.3	910.0	911.6	915.0	913.7
5087	950.0	951.3	960.0	961.2	999.0	996.9	1028.0	1030.7	993.0	995.7	1025.0	1027.3	1023.0	1024.8

TABLE X

p-*Ethoxyphenylimino*-d-*camphor* (m.p. 112°).

Solvents :	MeOH		EtOH		Acetone		Pyridine		Et acetate		$CHCl_3$		Benzene	
Conc. (g./100 c.c.) :	0.2500		0.2500		0.5000		0.2500		0.2500		0.2500		0.5000	
Calc. $[\alpha]_{\lambda}^{35} =$	$\frac{182.56}{\lambda^2-0.1734}$		$\frac{185.16}{\lambda^2-0.1724}$		$\frac{182.84}{\lambda^2-0.1713}$		$\frac{196.816}{\lambda^2-0.1774}$		$\frac{185.21}{\lambda^2-0.1702}$		$\frac{195.04}{\lambda^2-0.1771}$		$\frac{192.51}{\lambda^2-0.1796}$	
λ_0(Å) =	4164		4153		4139		4212		4126		4209		4239	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	660.0	660.0	667.0	667.0	656.0	656.0	722.0	722.0	662.0	661.9	718.0	718.0	712.0	711.9
6438	758.0	757.2	766.0	764.8	753.0	751.8	832.0	830.1	756.0	758.1	824.0	825.4	820.0	819.5
6104	914.0	916.9	924.0	925.3	907.0	908.7	1008.0	1008.8	918.0	915.5	1004.0	1002.8	996.0	997.9
5893	1050.0	1050.4	1058.0	1059.3	1040.0	1039.5	1158.0	1159.1	1046.0	1046.4	1152.0	1151.9	1148.0	1148.6
5780	1136.0	1136.0	1146.0	1145.1	1123.0	1123.1	1256.0	1256.0	1130.0	1130.0	1248.0	1248.0	1246.0	1246.0
5468	1452.0	1453.5	1460.0	1462.6	1430.0	1431.8	1620.0	1618.6	1440.0	1437.9	1604.0	1607.4	1613.0	1612.3
5461	1464.0	1462.8	1472.0	1471.9	1441.0	1440.8	1628.0	1629.3	1448.0	1446.9	1618.0	1618.0	1621.0	1623.2
5209	1862.0	1864.7	1872.0	1872.2	1830.0	1828.4	...	...	1830.0	1831.9	2082.0	2080.0	2102.0	2099.3
5087	2144.0	2140.2	2148.0	2145.5	...	...	...	...	...	...	2398.0	2401.2	...	...

Dimorphic Forms

The *p*-methoxyphenylimino-*d*-camphor exists in two dimorphic forms as described before (this *Journal*, 1958, **35**, 103). We have found the rotatory dispersion of both the forms to be the same, within limits of experimental error. These forms therefore behave similarly in solution (Tables III and IV).

EXPERIMENTAL

The compounds studied here were prepared and purified as described earlier (*loc. cit.*). The rotatory dispersion was determined in a 2 dm jacketed polarimeter tube. Water at 35° was kept circulating through the jacket. The observations are recorded in Tables I to X.

The authors wish to thank the Benaras Hindu University for providing research facilities and the Scientific Research Committee, Uttar Pradesh, for the grant of a research scholarship to one of them (B. S. Saxena).

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STUDIES ON THE RELATION BETWEEN CHEMICAL CONSTITUTION AND ULTRAVIOLET ABSORPTION SPECTRA OF OPTICALLY ACTIVE AND RACEMIC COMPOUNDS. PART IV. CORRELATION OF ABSORPTION MAXIMA AND CHARACTERISTIC WAVE-LENGTHS OF SOME ARYLIMINO- AND ARYLAMINO-CAMPHOR DERIVATIVES

By Bawa Kartar Singh and Bhupendra Sahai Saxena

The ultraviolet absorption spectra of *p*-sulphonamido-, *o*-, *m*-, *p*-methoxyphenylimino-camphors (*d*- and *dl*-) and *o*- and *p*-methoxyphenylamino-camphors (*d*- and *dl*-) have been taken with a view to comparing the 'characteristic' wave-lengths (λ_0s), deduced from Drude's rotatory dispersion equation, with absorption maxima (λ_{max}), obtained by direct measurement. The rotatory dispersion of these compounds is *simple*, being represented by Drude's 'one-term' equation, and there is one 'characteristic' wave-length governing rotation for each of these compounds. The ultraviolet absorption spectra of these compounds generally show two absorption maxima, and the one near the 'characteristic' wave-length is found to differ widely from it. The differences between λ_0 and λ_{max} range from 0.2 mμ to 83 7 mμ. An explanation of this discrepancy has been given. The nature of the racemic modifications has also been discussed.

In continuation of Parts I and II of this series (Singh and Miss Amma, *J. Sci. Ind. Res.*, 1957, **16B**, 202) we have determined the ultraviolet absorption spectra of *p*-sulphonamido-, *o*-, *m*-, *p*-methoxy-phenylimino *d*-camphors and *o*- and *p*-methoxy-phenylamino-*d*-camphors and compared the 'characteristic' wave-lengths, calculated from Drude's rotatory dispersion equation, with the absorption maxima obtained by direct measurements.

The absorption measurements of the racemic forms of these compounds have also been taken to throw further light on the nature of these racemic modifications investigated by us earlier (Singh and Saxena, this *Journal* 1958, **35**, 103) by the application of melting point—composition method of Roozeboom.

Experimental

The compounds studied here were prepared and purified according to the methods already described (*loc. cit.*).

The absorption spectra were recorded in very dilute solutions of the compounds in spectroscopically pure solvents with a Beckman DU spectrophotometer. The molecular extinction coefficients were calculated from optical density at different wave-lengths, but their peak values (ϵ_{max}) corresponding to the absorption maxima, λ_{max}, only have been recorded in Table I.

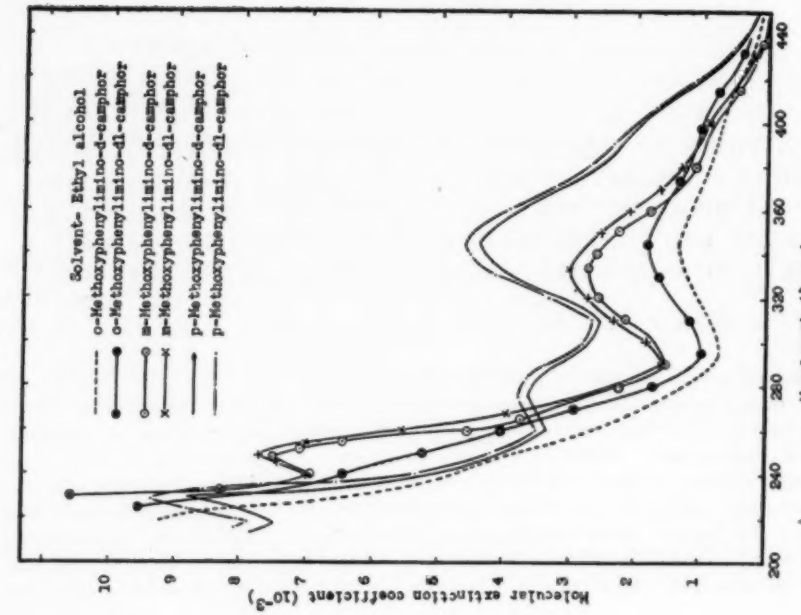

Solvent- Ethyl alcohol
o-Methoxyphenylimino-d-camphor
o-Methoxyphenylimino-dl-camphor
m-Methoxyphenylimino-d-camphor
m-Methoxyphenylimino-dl-camphor
p-Methoxyphenylimino-d-camphor
p-Methoxyphenylimino-dl-camphor
Molecular extinction coefficient (10^{-3})
Wavelength (λmμ)

FIG 2

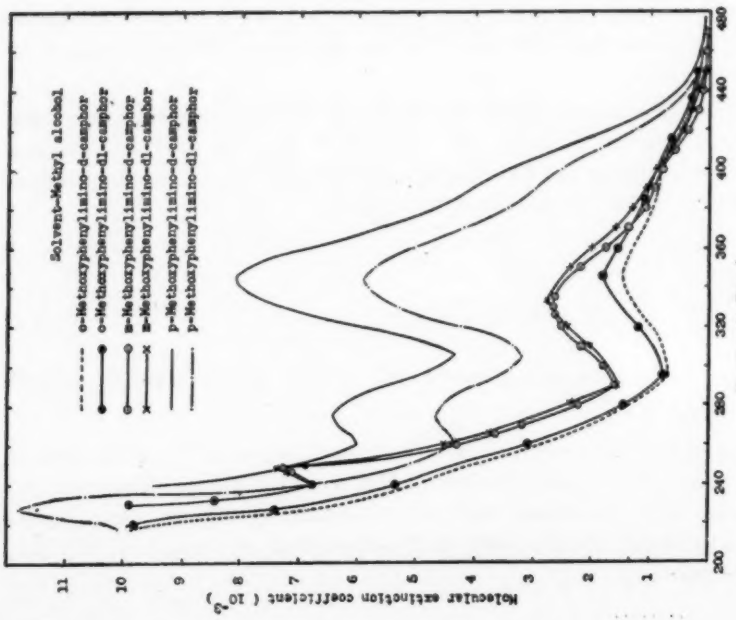

Solvent-Methyl alcohol
o-Methoxyphenylimino-d-camphor
o-Methoxyphenylimino-dl-camphor
m-Methoxyphenylimino-d-camphor
m-Methoxyphenylimino-dl-camphor
p-Methoxyphenylimino-d-camphor
p-Methoxyphenylimino-dl-camphor
Molecular extinction coefficient (10^{-3})
Wavelength (λmμ)

FIG. 1

FIG. 4

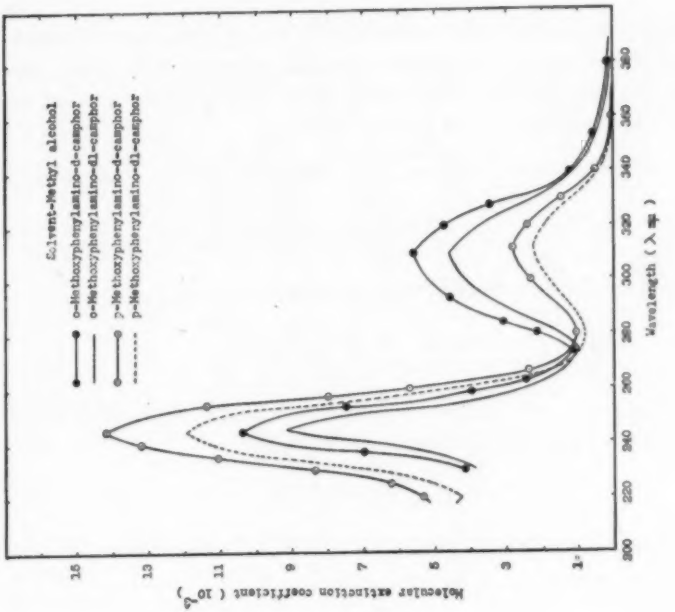
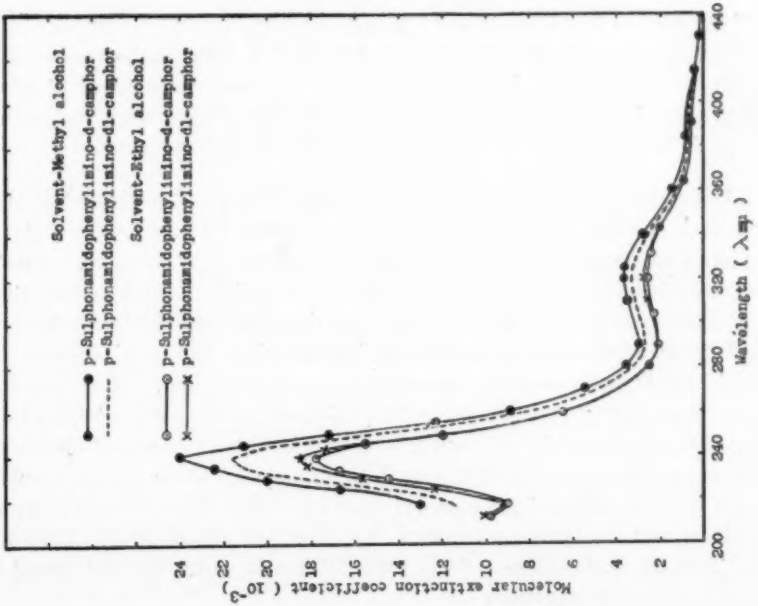

Solvent-Methyl alcohol
o-Methoxyphenylamino-d-camphor
o-Methoxyphenylamino-dl-camphor
p-Methoxyphenylamino-d-camphor
p-Methoxyphenylamino-dl-camphor
Molecular extinction coefficient (10^3)
Wavelength (mμ)

FIG. 3


Solvent-Methyl alcohol
p-Sulphonamidophenylamino-d-camphor
p-Sulphonamidophenylamino-dl-camphor
Solvent-Ethyl alcohol
p-Sulphonamidophenylamino-d-camphor
p-Sulphonamidophenylamino-dl-camphor
Molecular extinction coefficient (10^3)
Wavelength (mμ)

The ultraviolet absorption curves (Figs. 1 to 5) have been obtained by plotting the molecular extinction coefficients against wave-lengths and are shown only for methyl alcohol and ethyl alcohol ; those for chloroform, being similar to those in alcohols, have been omitted to economise space.

Discussion

The rotatory dispersion equation of Drude,

$$[\alpha]_\lambda = \sum \frac{K}{\lambda^2 - \lambda_\circ^2},$$

relating specific rotatory power, $[\alpha]\lambda$, to wave-length, λ, at which it is determined, contains several terms in the summation, namely,

$$K'/\lambda^2 - \lambda_\circ'^2,\ K''/\lambda^2 - \lambda_\circ''^2,\ K'''/\lambda^2 - \lambda'''^2_\circ \text{ etc.}$$

The characteristic wave-lengths, $\lambda'_\circ$, $\lambda_\circ''$, $\lambda_\circ'''$ represent the absorption bands which control rotation.

Since about 1912 this equation in its simplest form,

$$[\alpha]_\lambda = \frac{K}{\lambda^2 - \lambda_\circ^2},$$

has been used to test its validity by several workers, specially Lowry *et al.* (*Phil. Trans.*, 1927, **226A**, 391 ; *J. Chem. Soc.*, 1924, **125**, 1593). Whereas Lowry has shown that the rotatory dispersion could be represented by a very few Drude terms, Condon (*Rev. Mod. Phys.*, 1937, **9**, 432) regards these Drude terms as having average values resulting from the combination of several terms of more fundamental significance.

Generally in the case of organic compounds, the rotatory dispersion is expressed by 'one-term' (*simple dispersion*) or 'two-terms' (*complex dispersion*) formula. The remaining terms are neglected either because they are too small or nearly cancel each other. The terms found necessary in one- or two-term equation of Drude, within limits of experimental error, thus approximately represent the main contribution to the optical activity. Expressing the rotatory dispersion by 'one-term' or 'two-term' formula in this way, it therefore only approximately represents the optical rotation. Moreover, the very small range (670.8 to 520.9 mμ for the yellow-coloured compounds and 670.8 to 435.8 mμ for the colorless compounds) of the spectrum which we have employed for the determination of rotatory dispersion does not show the discrepancies in the values calculated from one- or two-term formula and the observed values of rotatory power. It is for these reasons that there are discrepancies between the observed values of the absorption maxima, λ_{max} , and the values of the *'characteristic'* wave-lengths, $\lambda_\circ$s, calculated from Drude's rotatory dispersion equation.

TABLE I

	Camphor derivatives.	Conc. (g./litre)	Solvents.	*d*-Isomer. $\lambda_{max.}$	*d*-Isomer. $\epsilon_{max.}$	*dl*-Isomer. $\lambda_{max.}$	*dl*-Isomer. $\epsilon_{max.}$	λ_o from Drude's one-term equation. *	λ_o-$\lambda_{max.}$
1.	*o*-Methoxyphenylimino-	0.04	MeOH	345 mμ	1466.0	345mμ	1860.0	359.1	14.1
		0.05	EtOH	345	1341.5	344	1815.7	371.0	26.0
		0.04	$CHCl_3$	345	1287.3	345	1646.3	364.7	19.7
2.	*m*-Methoxyphenylimino-	0.04	MeOH	330	2676.1	333	2777.8	398.3	68.3
				248	7317.0	248	7418.6		
		0.04	EtOH	333	2710.0	333	3042.0	397.5	64.5
				248	7533.8	248	7736.5		
		0.04	$CHCl_3$	333	3082.6	333	3109.7	399.3	66.3
				248	9024.3	248	9112.4		
3.	*p*-Methoxyphenylimino-	0.04	MeOH	345	8129.9	344	5907.8	408.8	63.8
				275	6427.2	275	4661.2		
						228	11788.5		
		0.04	EtOH	345	4390.2	345	4600.2	410.4	65.4
				275	3638.2	275	3794.0		
				230	8827.8	228	9403.7		
		0.04	$CHCl_3$	345	3965.6	345	4679.3	417.4	72.4
				275	3739.8	275	4245.7		
4.	*p*-Sulphonamidophenyl-imino-	0.04	MeOH	320	3696.0	320	3320.0	398.5	78.5
				240	24000.0	240	21600.0		
		0.04	EtOH	320	2624.0	320	2752.0	397.6	77.6
				240	17776.0	240	18560.0		
		0.04	$CHCl_3$	320	2656.0	320	2664.0	403.7	83.7
				248	17600.0	...	...		
5.	*p*-Methoxyphenylamino-	0.05	MeOH	312	2828.3	312	2266.0	245.2	0.2
				245	14196.0	245	11957.4		
		0.05	EtOH	312	2310.2	312	2722.2	263.5	17.5
				246	11990.0	245	12434.0		
		0.05	$CHCl_3$	312	2980.4	312	2352.6	302.6	—9.4
6.	*o*-Methoxyphenylamino-	0.05	MeOH	...	...				
				310	5632.0	310	4625.0	208.8	—36.2
		0.05	EtOH	245	10405.0	245	9170.0		
				310	5508.4	310	4810.2	234.3	—10.7
				245	10112.0	246	9600.0		
				228	4210.0	228	4190.0		
		0.05	$CHCl_3$	310	5880.4	310	5742.5	285.1	—24.9
				245	12228.0	246	11020.4		

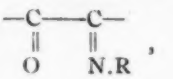
* Singh and Saxena, this *Journal*, 1958, **38**, 103.

We may now specifically discuss the absorption spectra of arylimino- and arylamino-camphors investigated by us.

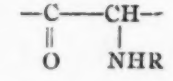
The *o*-methoxyphenylimino-camphors show absorption maxima at 345 mμ in all the three solvents. The *para* isomer also shows this band and a second band at 275 mμ in these solvents except that it shows also a third band at about 230 mμ in methyl alcohol and ethyl alcohol. In the case of the *meta* isomer, the 345 mμ band has shifted to 333 mμ and there is the second band at 248 mμ. In the *p*-sulphonamidophenylimino-camphors, the longer wave-length band has shifted to 320 mμ and the second absorption

maximum occurs at 240 mμ except in chloroform solution, in which it occurs at 248 mμ. In the case of *o*- and *p*-methoxyphenylamino-camphors, the longer wave-length band occurs at 310-312 mμ besides a second band at 245 mμ. The *o*-methoxyphenylamino-camphors show a third band at 228 mμ in ethyl alcohol.

The above analysis thus indicates that the conjugated chromophore,

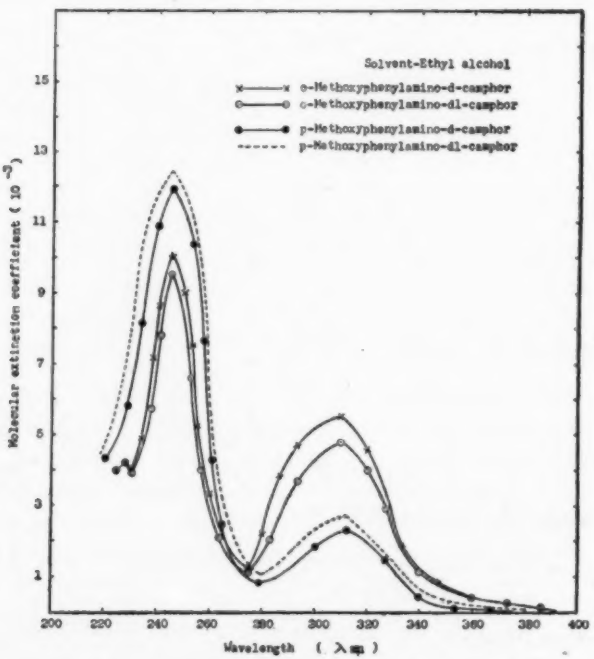


exhibits an absorption maximum, λ_{max}, at 345 mμ, but it has shifted to 310 – 312 mμ in the case of the corresponding amino compounds with the new chromophore,



The lower bands at 228 mμ to 248 mμ belong to the saturated molecules.

FIG. 5



The 'characteristic' wave-lengths in the case of *o*-methoxyphenylimino-*d*-camphor vary from 359 mμ to 371 mμ in the three solvents, whereas those for the *meta* and *para* isomers and *p*-sulphonamidophenylimino-*d*-camphors lie between 397 5 and 417.4 mμ. These results are in agreement with those obtained by Singh and Miss Seth (this

Journal, 1956, **33**, 821) for phenyl- and chlorophenyl liminocamphors. They found that the values of the λ_os of these arylimino compounds varied from 390 mμ to 400 mμ except in the case of *ortho* compound in which it was about 363 mμ and those for the corresponding arylamino compounds fluctuated between 280 and 290 mμ.

We thus find similar results in the case of methoxy- and *p*-sulphonamido phenyliminocamphors, but the values found by us for the methoxyphenylamino-camphors are somewhat lower than those found for the analogous chlorophenylamino-camphors.

The 'characteristic' wave-lengths (λ_os) deduced from Drude's 'one-term' equation, thus, differ from the absorption maxima, λ_{max} (Table I). This difference varies from 0.2 to 83.7 mμ, it being more in the aryl*imino* than in aryl*amino* compounds. This may be explained by reasons given above.

Racemic Forms.—The ultraviolet absorption spectra of the racemic forms are found to be almost identical with those of the corresponding *dextro* forms, the differences being in the molecular extinction coefficients in the two cases.

Since the ultraviolet absorption curves of the *dextro* and *laevo* isomers of the substances are always identical, the curves for the racemic forms must also be the same if the latter occur as a mixture of the *d* and *l* forms. However, if the racemic form in solution is a racemate (*dl*-compound), its absorption curve may or may not be identical with that given separately by the antipodes.

In the solid state all these racemic forms were found to be racemic compounds (Singh and Saxena, *loc. cit.*) by the melting point—composition method of Roozeboom. Since in very dilute solutions they give curves almost identical and nearly superposable with those given by the *dextro*- forms, it may be concluded that they are almost completely dissociated in dilute solution into the optically active and opposite forms.

Further investigation in this direction, using concentrated solutions, could not be made as the solutions of even twice this strength became opaque and unsuitable in the required range of the spectrum.

The authors thank the Banaras Hindu University for providing research facilities and the Scientific Research Committee, Uttar Pradesh, for the grant of a research assistantship to one of them (B.S. Saxena).

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IMPORTANT SIGNIFICANCE OF S-SHAPED CURVES DURING SLOW COAGULATION OF LYOPHOBIC SOLS

By Amal K. Bhattacharya and Abani K. Bhattacharya

The points of inflection in the S-shaped curves of slow coagulation may be assumed to denote the same kinetic state of aggregation when the sol is coagulated with different concentrations of the electrolyte, because at this stage $d^2x/dt^2 = 0$ for all cases. The times corresponding to the points of inflection for different concentrations of the electrolyte, KNO_3 (Kruyt and Troelstra's extinction data), added to the sol of AgI, satisfies the linearity of the equation

$$\frac{1}{C-a} = \frac{n}{m}.t + \frac{1}{m}$$

which follows from the empirical relation given by

$$C = a + \frac{m\left(\frac{1}{t}\right)}{n + \frac{1}{t}}.$$

In a previous paper on the verification of the above equation by different techniques (*J. Colloid Sci.*, 1956, **11**, 124) it was shown that the relation between the concentration of the electrolyte and the time of coagulation as given by the equation,

$$C = a + \frac{m\left(\frac{1}{t}\right)}{n + \frac{1}{t}}$$

(where C is the concentration of the electrolyte, t is the time for the same degree of aggregation or coagulation, and a, m and n are the parametric constants), was supported by the experimental data obtained from the variations in (*i*) viscosity, (*ii*) light transmission, (*iii*) extinction coefficient and (*iv*) counting of the number of particles and tyndallometric data. The data in respect of the variations of the foregoing properties were taken from the observations of Gann (*Koll. Chem.-Beih.*, 1916, **8**, 64), Mukerjee (*J. Chem. Soc.*, 1924, **125**, 785), Kruyt and Troelstra (*Kolloid Beih.*, 1945, **54**, 225) and Tezak (*J. Phys. Coll. Chem.*, 1951, **55**, 1557). The same stage of coagulation, or more correctly the same degree of aggregation, was obtained, *a fortiori*, by drawing a line parallel to the time axis to cut the characteristic curves for the different concentrations of the added electrolyte. This line would cut the family of curves (one curve for each different concentration of the electrolyte) and, hence, it could be reasonably assumed that the same value of viscosity, light extinction or transmission, or number of particles would mean the same state of coagulation or degree of aggregation. The constant 'a' was determined by extrapolation of $C - (1/t)$ curves as explained before, and the linearity of the relation between $1/(C-a)$ and t was found to hold good in the light of the equation.

It was emphasised further by us (*Kolloid Z.*, 1955, **141**, 95 ; 1956, **148**, 136) that the points of inflection in the autocatalytic viscosity—time curves of As_2S_3 and $Fe(OH)_3$ sols denoted the same kinetic stage of slow coagulation for the different concentrations of an electrolyte added to the sol. The times corresponding to the points of inflection in the viscosity—time curves, when plotted against the respective values of $1/(C-a)$, gave a straight line, which proved the validity of the equation.

Kruyt *et al.* (*loc. cit.*) studied the coagulation of silver iodide sol by measuring the changes in the extinction of light and obtained autocatalytic curves when the % extinction was plotted against the concentration of the coagulating electrolyte (potassium nitrate) for different times of coagulation (Kruyt, "Colloid Science", 1952, p. 299). The values of the %extinction obtained at the points of inflection of these S-shaped curves, reported in this communication, also confirm the linearity of the relation between $1/(C-a)$ and t.

Method of Verification.—In order to obtain the values of t, C and the constant a, the concentration 'C' corresponding to the inflection points of the curves was read. The time during which coagulation had proceeded was given; C was then plotted against $1/t$. The curve on extrapolation cuts the C-axis when $1/t = 0$ (Fig. 1). The intercept on the C axis gives the value of a. Then $1/(C-a)$ was plotted against t and a straight line was obtained (Fig. 2).

TABLE I

$a = 120$ mM/litre. $m = 41.7$ mM/litre. $n = 29.19$ min.$^{-1}$

C.	t.	$1/t$.	$C-a$.	$1/(C-a)$.
132.4 m M/litre	8 mins.	0.125	12.4	0.08065
136.3	5	0.200	16.3	0.06135
142.2	3	0.333	22.2	0.04505
146.1	2	0.500	26.1	0.03831
152.0	1	1.000	32.0	0.03125

FIG. 1

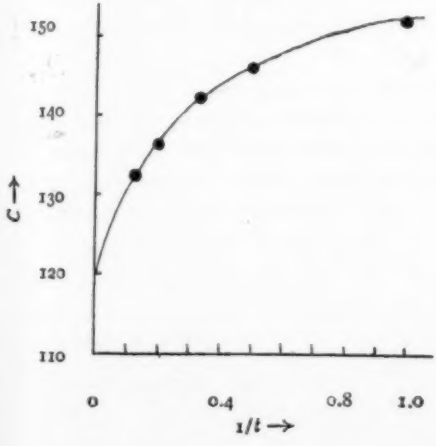
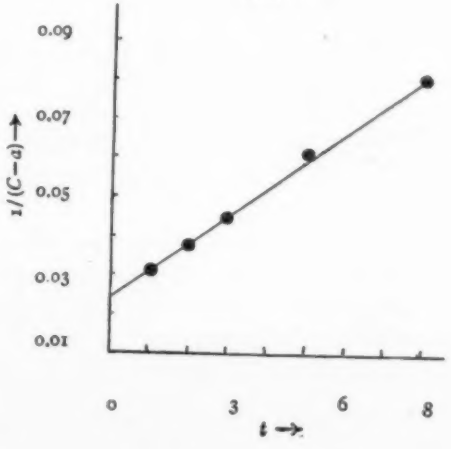


FIG. 2



In the light of our observations previously communicated (*loc. cit.*) and the results derived from the extinction curves, it may be emphasised, *a priori*, that the points of inflection in the S-shaped curves of slow coagulation with different concentrations of an electrolyte denote the same characteristic state in the kinetics of the process, where d^2x/dt^2 becomes zero. It may be visualised therefore that at this stage of aggregation, the system is governed by such conditions as to reduce the acceleration of the change to zero. To reach this state under the influence of varying concentrations of the electrolyte, different times will be required, which fit in the equation under reference very satisfactorily. This fact was evidenced by our study of the slow coagulation of As_2S_3 and Fe $(OH)_3$ sols by viscosity measurements, and it was again supported by the data obtained from the extinction curves of AgI sol, given by Kruyt and Troelstra (*loc. cit.*).

In view of the above observations it may be concluded that the inflection points of the S-shaped curves of slow coagulation indicate a very characteristic state in the mechanism of slow coagulation and serve as a strong evidence to prove the validity of the equation referred to above.

The constants a, m and n of the equation were evaluated graphically as explained previously (this *Journal*, 1952, **29**, 759) and their values have been shown in Table I.

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SPECTROPHOTOMETRIC AND ELECTRICAL CONDUCTANCE STUDIES IN THE FORMATION OF IRON^{III}-AMMONIUM AURINTRICARBOXYLATE CHELATE

By Anil K Mukherji* and Arun K. Dey

The formation of a coloured chelate, having λ_{max} at 560 mμ, between ferric ion and ammonium aurintricarboxylate has been reported. It has been found that only one complex having the ratio 1:1 is formed in solution. Job's method of continued variation, using spectrophotometric and electrical conductance measurements, has been employed. The p_H of the system is not affected by chelation, showing that the phenolic hydrogens do not take part in the chelation process. The structure therefore has been suggested to involve a chelation between the quinoid oxygen and the adjacent carboxylic oxygen.

The spectrophotometric data have been used to calculate the formation constant, which works out to be 4.8×10^4 at 25°, while the free energy of formation is -6.4 Kcals.

Ammonium aurintricarboxylate, commonly known as Aluminon, has been employed for the colorimetric determination of aluminium (Johnson, "Organic Reagents for Metals", Chemical Publishing Co. Inc., New York, 1955), including the estimation of the metal in commercial materials and alloys (Banerjee, *Anal. Chem.*, 1957, **29**, 55 ; Bobtelsky and Ben Basset, *Anal. Chim. Acta*, 1956, **14**, 439). Recently, Mukherji and Dey (*Z. anal. Chem.*, 1956, **152**, 424) have reported the formation of coloured lakes of various inorganic cations with ammonium aurintricarboxylate and suggested further use of this compound in colorimetric analysis of cations. They have studied the formation and stability of metal chelates, viz., those of copper, uranium, beryllium and of thorium (under publication elsewhere). Dey and Mukherji have also been able to utilise the colour formation in the micro-determination of copper, beryllium and iron (*Proc. Natl. Acad. Sci., India*, 1957, **26A**, 138) and thorium (unpublished).

Smith *et al.* (*J. Res. Natl. Bur. Standards*, 1938, **21**, 105 ; *Anal. Chem.*, 1949, **21**, 1334) observed that in order to obtain a stable colour the addition of alkali must be avoided. Mukherji and Dey (unpublished work) from electrical conductance studies found the reagent to behave as a colloidal electrolyte and recommended that physico-chemical measurements of complexes involving Aluminon should preferably be carried out in dilute solutions.

In this paper we have presented our results on the spectrophotometric and electrical conductance studies on ferric chloride-ammonium aurintricarboxylate system, in order to elucidate the composition and stability of the chelate formed in solution.

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Experimental

Solutions of ferric chloride (BDH-Analar) and of ammonium aurintricarboxylate (BDH-Reagent) were prepared in double distilled water and standardised as usual. The Aluminon used was prepared by the method of Smith *et al.* (*loc. cit.*) as was ascertained from the manufucturers (British Drug Houses Ltd., Poole, *private communication*, December 1956). All solutions employed were always freshly prepared ones.

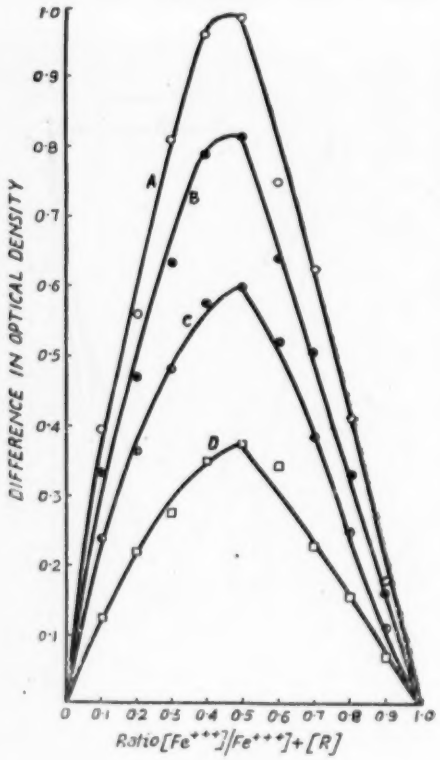
Optical measurements were made with a Unicam SP 500 spectrophotometer, using glass absorption cells of 10 mm light path, supplied by the manufacturer. The experiments were carried out in an air-conditioned room maintaining 25°. The individual solutions were kept in a thermostat maintained at 25° ± 0.01° and the mixtures were allowed to stand for 15 minutes in the thermostat to attain equilibrium.

For the measurement of electrical conductance, L & N Kohlrausch slidewire with an audiofrequeney oscillator was employed. The conductivity cell was of the dip type, having a cell constant 0.132. The solutions and the mixture were kept in an electrically operated T & M Precision thermostat, maintaining a temperature of 32° ± 0.01°, before and during measurements. The total volume was kept 50 c.c. in every case. The p_Hs were measured with L & N p_H-meter operated on 220 volts/50 cycles mains, using a glass electrode supplied with the instrument.

Nature of Complexes Formed.—Mixtures containing varying proportions of ferric chloride and ammonium aurintricarboxylate were prepared and the optical densities at different wave-lengths measured. In each mixture λ_{max} was observed at 560 mμ, showing that the nature of the complex species in all the mixtures was identical. Thus, it may be concluded that only one complex is formed in all the cases investigated.

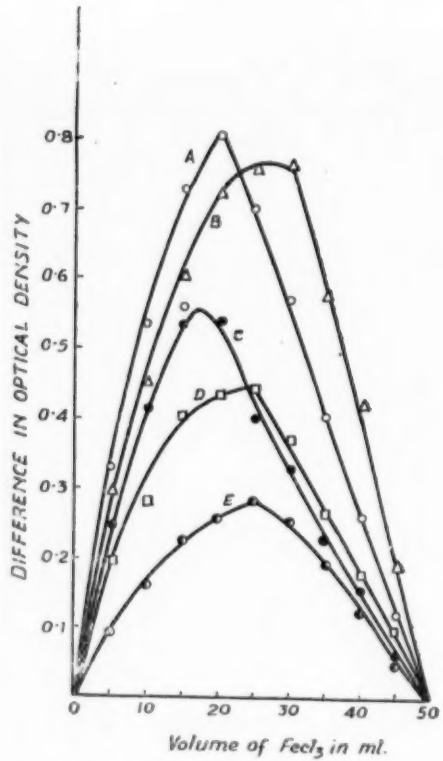
Stoichiometry of the Components.—The composition of the complex was determined by Job's method of continued variation (*Compt. rend.*, 1925, **180**, 928; *Ann. chim.*, 1928, *x*, **9**, 113; cf. Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437; 1942, **64**, 1630). The total volume in each case was 50 c.c. Optical densities were measured at 560, 540, 460 and 440 mμ. It may be mentioned that at the dilutions and spectral regions employed, ferric chloride solutions have no absorption. The results are represented graphically in Figs. 1-4. In the figures, the difference of optical density of the mixture and that which would be shown by the reagent above, if no chelation occurs, is plotted against the composition of the mixture. The results of electrical conductance studies are plotted in Fig. 5. Here too, the difference in observed conductance of the mixture and that expected in case of no reaction between the metal ion and the reagent, is plotted against the composition of the mixture. In the legends, c represents the concentration of ferric chloride, while that of ammonium aurintricarboxylate, *i.e.*, $p = c'/c$.

FIG. 1



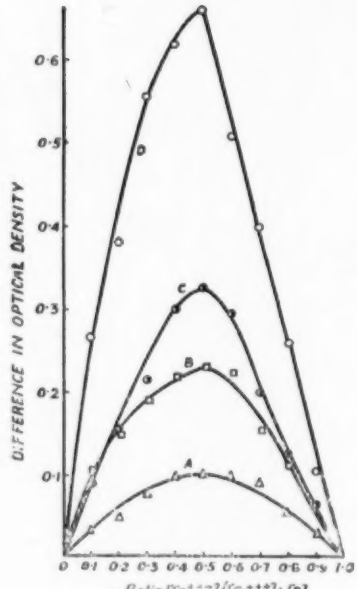
λ=560 mμ. p =1.
Curve A: c =2.5×10^{-4} M
B: „ =2.0× „
C: „ =1.66× „
D: „ =1.0× „

FIG. 2



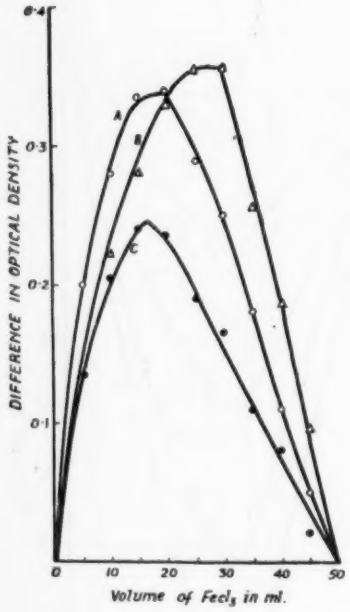
λ=560 mμ : A: c =2.5×10^{-4}M; p=0.66
„ B: c =1.66 „ p=1.5
„ C: c =2.0× „ p=0.55
λ=460 D: c =2.5× „ p=1
„ E: c =1.66× „ p=1

FIG. 3



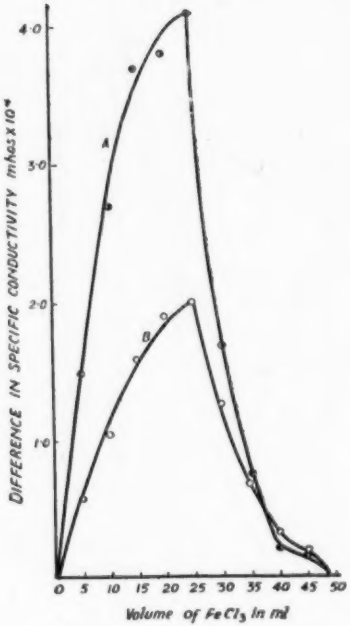
λ=440 mμ. p=1.
A: c=1.0×10^{-4}M
B: c=2.0× „
λ=540 mμ. p=1.
C: c=1.0×10^{-4}M
D: c=2.0× „

FIG. 4



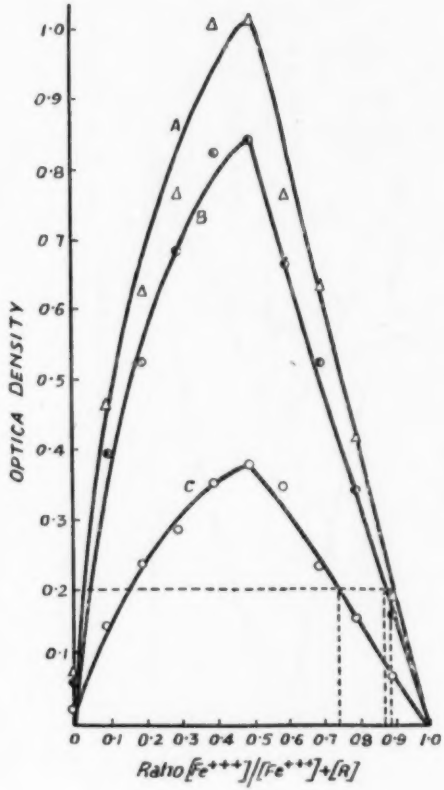
λ=460 mμ.
A: $c = 2.5 \times 10^{-4} M$; $p = 0.66$
B: $c = 1.66 \times$,, ; $p = 1.5$
C: $c = 2.0 \times$,, ; $p = 0.5$

FIG. 5



Curve A: $c = 1.0 \times 10^{-3} M$; $p = 1$.
B: $c = 0.5 \times 10^{-3} M$; $p = 1$.

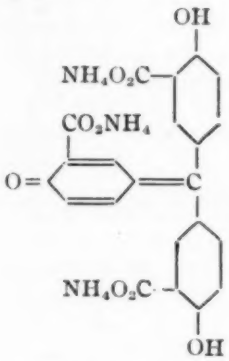
FIG. 6



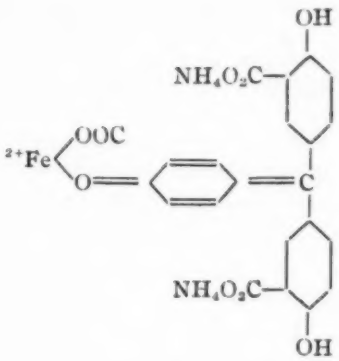
λ=560 mμ; $p = 1$.
A: $c = 2.5 \times 10^{-4} M$
B: $c = 2.0 \times$,,
C: $c = 1.0 \times$,,

DISCUSSION

It may be seen from the figures that in every case the peaks of the curves occur at a ratio of 1 : 1 of the reactants. It has also been found by p_H measurements that the acidity of the system does not increase on mixing solutions of ferric chloride and ammonium aurintricarboxylate. This shows that hydrogen ions are not liberated as a result of chelation and, hence, the phenolic hydrogen does not take part in the reaction. It may therefore be concluded that the chelation occurs between the quinoid oxygen and the adjacent carboxylic oxygen, as shown below :



(I) Chelating agent.



(II) Iron^{III} chelate.

For the calculation of the formation constant, we have employed the optical density data and have followed the method described by Mukherji and Dey (this *Journal*, 1957, **34**, 461). The method of continued variation was employed and optical densities of mixtures of various compositions were measured at a fixed wave-length. The observed optical density has been plotted against [M]/[M]+[R] ([M]=concentration of metal ion and [R] that of chelating agent). In Fig. 6, such a graph is shown for the system investigated. In our case, the metal ion is colorless (at the concentrations and wave-lengths used), while the chelating agent is coloured. Hence, with the progressive addition of metal ions, [R] decreases, and it may be assumed that in the descending portions of the curves, where the metal ions are in large excess, most of the chelating agent is bound up in the complex. Therefore, in this portion of the curve, optical density of the free chelating agent does not contribute substantially to the optical density of the system. The observed optical density may, hence, be regarded as the colour of the complex alone. Thus, in Fig. 6, in curves A, B and C, where the optical densities are the same, (say 0.2), the respective amounts of the complex may be taken to be identical.

In the system, where an 1 : 1 complex is formed,

$$mA + nB \rightleftharpoons A_mB_n$$

i.e., $m=n=1$, the formation constant,

$$K = \frac{x}{(a - x)(b - x)} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where x = concentration of the complex at equilibrium, and a and b are initial concentrations of the metal ion and the chelating agent respectively. Taking two concentrations a_1, a_2 and b_1, b_2 of the reactants, having the same optical density, *i.e.*, the same value of x, we have

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \quad \ldots \quad \ldots \quad (2)$$

or $$x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Knowing the value of x from equation (3), the value of K can be found out by substitution in equation (1).

We have calculated the value of the formation constant of ferric ammonium aurintricarboxylate chelate to be 4.8×10^4.

The free energy of formation of the chelate has been calculated with the help of the expression :

$$\Delta F^\circ = -RT \ln K \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

where ΔF° is the standard free-energy change, R, the gas constant and T, the absolute temperature.

The free energy of formation of ferric ammonium aurintricarboxylate works out to be -6.4 Kcals. at 25°.

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STUDIES ON THE METAL COMPLEXES OF HYDROXAMIC ACIDS. PART II. COLOURED COMPLEXES OF IRON, VANADIUM AND MOLYBDENUM WITH NICOTINOHYDROXAMIC ACID AND THEIR ANALYTICAL USES

By R. L. Dutta

Traces of iron (whether present initially as ferrous or ferric) has been determined spectrophotometrically by measuring the optical density of the golden yellow colour formed between the metal and nicotinohydroxamic acid at p_H 4.5 to 6.0 at 440 mμ (Sandell sensitivity 0.014 γ). The empirical compositions of the violet, red and the golden yellow coloured complexes of ferric iron have been determined by Job's method of continued variation, giving metal-ligand ratio of 1:1, 1:2 and 1:3 respectively.

Vanadium has been determined by measuring the optical density of the golden yellow complex formed between the metal and the reagent in 50% ethanol over the p_H range 2.5 to 4.5 at 440 mμ (Sandell sensitivity 0.014 γ). A solvent extraction procedure for its determination has also been described. The empirical compositions of a variety of coloured products formed between the metal and the reagent in aqueous and also in 50% ethanol medium have been determined (Job's method). The metal-ligand ratio for all is given by 1:3.

Molybdenum has been estimated by measuring the intensity of its yellow coloured complex with the reagent at 380 mμ or at 390 mμ over the p_H range 6.5 to 8.0. The composition of the complex has also been determined (Job's method). It gives a metal-ligand ratio of 1:2.

In a previous communication (Dutta, this *Journal*, 1957, **34**, 311), the nature and the analytical aspects of the colour reaction of traces of manganese with nicotino- and *iso*nicotino-hydroxamic acids in ammoniacal medium have been fully discussed. In this paper, the results of similar studies on the coloured complexes of iron, vanadium and molybdenum with nicotinohydroxamic acid have been recorded. The reagent also develops a yellow colour with titanium and uranium under suitable p_H, but the colours are not very sensitive.

Ferric iron develops with excess reagent a violet colour (absorption maximum 500mμ) at p_H 1.5 to 2.5, a red colour (absorption maximum 460/470 mμ) at p_H 2.8 to 3 and a golden yellow colour (absorption maximum 440mμ) at p_H 4.5 to 6. The last reaction is sensitive, and suitable for the colorimetric estimation of iron (Sandell sensitivity 0.014 γ). (Vanadium interferes seriously). Job's method indicates an 1:1 complex for the violet colour, an 1:2 complex for the red colour and an 1:3 complex for the golden yellow colour.

Ferrous iron develops an intense golden yellow colour with excess reagent above p_H 4.0. The absorption spectrum over the p_H range 4.6 to 6 is perfectly superimposable on that given by an equal amount of ferric iron with the reagent at the same p_H. This colour can be utilised for the colorimetric estimation of iron (Sandell sensitivity 0.014 γ). Ferrous iron does not give rise to the violet colour at lower p_H, characteristic of ferric iron, even on standing for hours. But, when the golden yellow

coloured complex, which is formed by the addition of ferrous iron to the reagent in near neutral or alkaline range, is brought to p_H 1.5 to 2 or to about 3, the same violet or red colour, characteristic of ferric iron, is developed. Das Gupta and Dhar (*J. Sci. Ind. Res.*, 1952, **11B**, 500, 520) report that oxalohydroxamic acid exhibits only a weak colour reaction with ferrous iron, whereas that with benzohydroxamic acid (Das Gupta and Singh, *ibid*, 1952, **11B**, 268) is quite strong. Salicylhydroxamic acid also develops an intense red to golden yellow colour with ferrous iron in alkaline medium. These facts probably suggest that in the near neutral to alkaline range, ferrous iron is oxidised to the ferric state almost instantaneously, whereas in strong acid solution, this oxidation of the complex does not occur to an appreciable extent. Job's method of continued variation between ferrous iron and the reagent at p_H 5.3 shows an 1 : 3 complex. Nicotinohydroxamic acid therefore appears to be a suitable colorimetric reagent for iron irrespective of the initial oxidation state of the metal.

Vanadium (added as vanadate) develops with the reagent a series of colours. In aqueous medium, a dull purple colour (absorption maximum 500 mμ) at a p_H of about 3, and a bright purple colour (absorption maximum 500-510 mμ) at a p_H of about 8 are formed. Neither of these two colours offers a suitable p_H range for colorimetric determination of vanadium, nor are they sensitive. On the other hand, in 50% alcoholic medium, there appears an intense golden yellow colour (absorption maximum 440 mμ) in acid medium and in alkaline medium, a bright purple colour (absorption maximum 500-510 mμ). The golden yellow colour is suitable for colorimetric estimation of traces of vanadium over the p_H range 2.5 to 4 5. The method is highly sensitive (Sandell sensitivity 0.014 γ). The dull purple colour formed in aqueous medium (p_H 3.1) can be extracted with *iso*amyl or *iso*butyl alcohol. The absorption spectrum of the extracted colour is similar to that of vanadium complex in 50% ethanol (absorption maximum 440 mμ, sensitivity 0.012 γ). Iron interferes seriously during the estimation of vanadium in 50% alcohol. However, in presence of uranium and molybdenum, vanadium can be estimated by extraction of the dull purple colour in aqueous medium with *iso*butyl or *iso*amyl alcohol. But iron interferes even by this procedure. These colour reactions are not shown by vanadium in presence of a large amount of reducing agent, such as hydroxylamine. Brandt and Wise (*Anal. Chem.*, 1955, **27**, 1392) also report that in the estimation of vanadium with benzohydroxamic acid, all the vanadium must be present in the quinquevalent state. These facts suggest that the coloured products of vanadium are derivatives of pentavalent vanadium. Job's method of continued variation shows both the dull purple and bright purple colours formed in aqueous medium correspond to 1 : 3 complexes. In 50% alcohol also, Job's variation indicates 1 : 3 complexes in acid as well as in alkaline medium. All the coloured products are weak complexes as is evident from the fact that a very large excess of the reagent (about 60-70 times the molar proportion of vanadium in 50% alcoholic medium) is necessary for complete colour formation. Das Gupta and Singh (*loc. cit.*) report an 1 : 1 complex for vanadium benzohydroxamic acid in 50% alcohol at p_H 3.0. Bhaduri and Rây (*Z. anal. Chem.*, 1957, **154**, 103) report an 1 : 1 complex for the blue colour produced by vanadium and salicylhydroxamic acid in aqueous medium

at p_H 3.0 to 3.8. They have also isolated a blue-black powder, having vanadium and the reagent in the ratio of 1 : 2, by working in a concentrated solution at about the same p_H. In the present case, all the soluble coloured products have been identified to have the same metal-reagent ratio. The acidic complex is extractable with higher alcohols whereas the coloured complex in alkaline range is non-extractable with organic solvents. Besides these coloured soluble products, a brownish black compound, having the metal-nicotinohydroxamic acid ratio as 1 : 1, has also been isolated by working in a concentrated solution at p_H about 3. This compound will be reported later.

Molybdenum (added as molybdate) develops with the reagent, an intense yellow colour which has been made the basis of colorimetric estimation of molybdenum over the p_H range 6.5 to 8. The colour has no absorption maximum in the visible region (sensitivity 0.026γ at 380mμ and 0.032γ at 390 mμ). Job's method indicates an 1 : 2 complex at this p_H range. Bhaduri and Rây (*loc. cit.*) report an 1 : 2 complex for the yellow colour formed between molybdenum and salicylhydroxamic acid at p_H 6.3 to 7. They have also isolated a yellow compound having molybdenum and the reagent in the ratio of 1 : 2 at p_H 3. Under suitable conditions, it has also been possible to obtain a yellow compound, which has the metal-nicotinohydroxamic acid ratio as 1 : 1. This compound will be reported in a subsequent communication.

EXPERIMENTAL

Fe^{III} solution was prepared from ferric nitrate ; its iron content was determined gravimetrically as oxide. Fe^{II} solution was prepared by weighing G. R. ferrous ammonium sulphate. Vanadium solution was prepared from Analar ammonium vanadate. Vanadium content was estimated gravimetrically as vanadium pentoxide. Molybdenum solution was prepared by weighing pure MoO_3, dissolving in alkali, neutralising and finally making up to a known volume. All the standard solutions were appropriately diluted.

Preparation of nicotinohydroxamic acid hydrochloride has been described earlier (Dutta, *loc. cit.*). 1% Reagent solution was used.

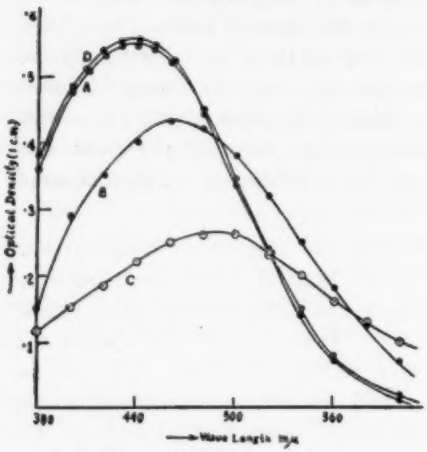
A Unicam SP 600 spectrophotometer was used for the measurement of optical density in 1 cm cells, unless otherwise mentioned. A Cambridge p_H-meter was used for the measurement of p_H.

In Figs. 1-3, the absorption spectra of iron (ferric and ferrous), vanadium (in aqueous as also in 50% ethanol medium) at different p_H values as well as that of molybdenum in presence of a large excess of the reagent are shown.

The golden yellow colour developed by iron was made use of for the colorimetric estimation of ferric or ferrous iron at p_H 4.5 to 6, optical density remaining constant over this p_H range. Colour intensity was measured at 440 mμ. For

FIG. 1

Absorption spectra.

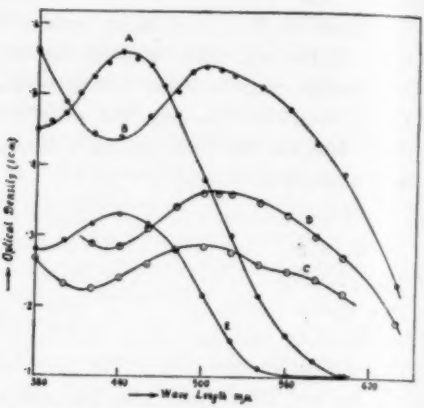


A. Fe^{3+}-nicotinohydroxamate (8γ Fe/c.c.) at p_H 5.4.
B. Do at p_H 3.0c.
C. Do at p_H 1.8.

D. Fe^{2+}-nicotinohydroxamate (8γFe/c.c.) at p_H 5.2.

FIG. 2

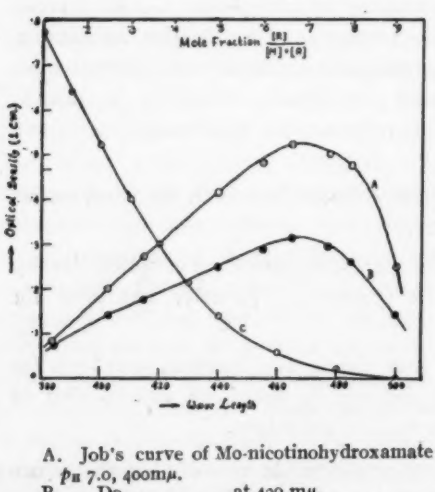
Absorption spectra.



A. Vanadium-nicotinohydroxamate (8γV/c.c.), in 50% ethanol at p_H 3.76.
B. Do at p_H 8.92.
C. Vanadium (8 γ/c.c.)-nicotinohydroxamate in aq. medium at p_H 2.9.
D. Do at p_H 8.0.
E. Amyl alcohol extract of aq. vanadium nicotinohydroxamate colour (p_H of the aqueous medium 3.06)(4γV/c.c.).

complete colour formation, an excess of the reagent, about 15-20 times the molar proportion of iron, is necessary. The colour is stable for about a day and then fades slowly. Beer's law is obeyed by both ferrous and ferric iron over the range 0.5 to 8γ iron (Fig. 4, curve 1). Sandell sensitivity is the same for both (0.014γ). The effect of diverse ions on the colour intensity has been fully investigated with respect to 4γ Fe/c.c. in a total volume of 25 c.c. (at p_H 4.5-5). Sulphate, chloride, nitrate, carbonate, borate, phosphate (150γ), tartrate (50γ), aluminium (40γ), zinc, cadmium, lead, tungstate, manganese, copper (100γ), nickel (150γ), cobalt (100γ), chromium (80γ) do not interfere. In presence of titanium (60γ), uranium (100γ) and molybdenum (100γ), the colour intensity should be measured at 500-520mμ, where absorption of the other coloured species is negligible. But serious interference is caused by citrate, oxalate and vanadium.

FIG. 3

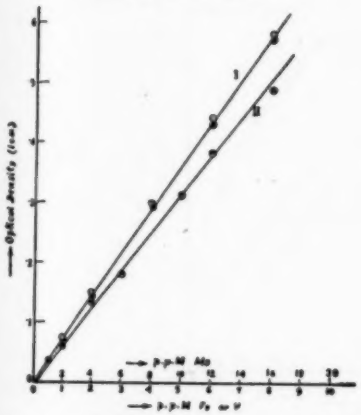


A. Job's curve of Mo-nicotinohydroxamate p_H 7.0, 400mμ.
B. Do at 420 mμ.
C. Spectra of molybdenum (20 γ/c.c.) nicotinchydroxamate, p_H 6.94.

The golden yellow colour developed by vanadium in 50% ethyl alcohol is highly sensitive and is suitable for the colorimetric estimation of the metal. Optical density of the colour remains constant over the wide range of p_H 2.5 to 4.5. The colour is perfectly stable. Beer's law is closely followed over the range 0.5 γ to 10 γ vanadium (Fig. 4, curve I). The optimum p_H for extraction of the aqueous colour is 3 to 4. The partition coefficient of the coloured product between water and the alcohol is not, however, highly favourable. Thus, it was felt necessary to extract the colour produced by 0.1 mg. vanadium at least three or four times by 5 c.c. portions of *iso*butyl alcohol and then making the volume to 25 c.c. Sandell sensitivity in 50% ethyl alcohol at 440 mμ, the optimum wave-length of measurement of the optical density, is 0.014γ and that by extraction procedure is 0.012γ at 440 mμ. A large excess of the reagent (at least 60-70 times the molar proportion of vanadium) is necessary for complete colour formation. The effect of diverse ions on the colour intensity has been fully studied with respect to 4γ V/c.c. in a total volume of 25 c.c. Ions such as nitrate, chloride, sulphate, borate, phosphate, acetate, thiocyanate, aluminium, cadmium, copper (80γ), nickel (100γ), cobalt (100γ), lead, zinc, chromium (80γ), manganese (120γ), mercury, thorium do not interfere. In presence of molybdenum (100γ) and uranium (50γ), the colour should be measured at 500-520 mμ. Citrate and iron interefere seriously. However, interference due to uranium and molybdenum can be eliminated by extraction procedure, but iron interferes as the iron hydroxamate complex is also partially extractable with higher alcohols.

FIG. 4

Beer's law curves.



I, ⊙ Fe^{3+}-nicotinohydroxamate colour at p_H 5.0, 440 mμ.

• V^{5+}. ,, at p_H 3.0 ,, (50% ethanol midium)

II. Mo^{6+} Nicotinohydroxamate colour at p_H 7.2, 390 mμ.

The optical density of the molybdenum nicotinohydroxamate colour remains constant over the p_H range 6.8 to 8. Optimum wave-lengths for measurement of optical density is 380mμ or 390mμ. The reagent solutions have slight absorption at these wave-lengths. Measurements should therefore be made against reagent blanks. A large excess of the reagent, at least 80 times the molar proportion of molybdenum, is required for maximum colour formation. Beer's law is perfectly obeyed over the range 2 to 20γ Mo (Fig. 4, curve II). Many metal ions and anions interfere, either due to strong absorption at that wave-length or due to precipitation of the metal hydroxides.

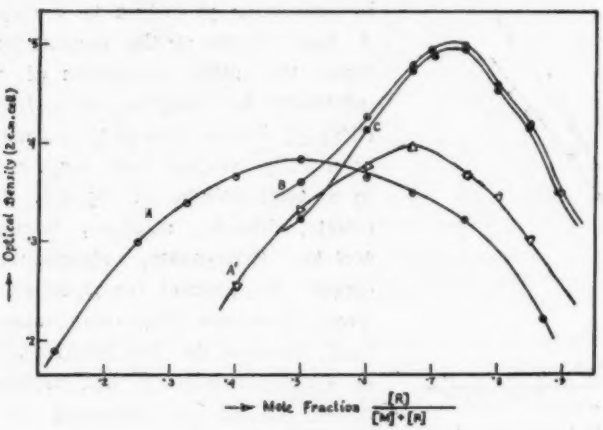
Determination of Empirical Composition of the Coloured Complexes by Job's Method

A. Iron Complexes.—For the violet ferric complex, 0.001*M* solutions of ferric nitrate and 0.001*M* nicotinohydroxamic acid hydrochloride solutions were mixed

(metal soln. + reagent soln. = 40 c.c.), p_H adjusted to 2, volume made up to 50 c.c. and the optical densities were then measured at 500 mμ and also at 550mμ in a 2 cm cell. Optical density plot against mole fraction of the reagent shows a maximum at 0.5, indicating an 1 : 1 complex between ferric iron and the reagent (curve A, Fig. 5). For the red ferric complex, a similar determination was made at p_H 3.01 and optical densities read at 470 mμ and at 500 mμ. Corrections for the colour developed by iron alone under similar conditions were made. Corrected optical densities (at 470 mμ) were plotted against mole fraction of the reagent (curve A′, Fig. 5). An 1 : 2 complex is thereby shown to exist.

FIG. 5.

Job's curves of iron nicotinohydroxamate.



A. Fe^{3+}-Reagent, p_H 2, 500mμ.
A′. Do p_H 3.01, 470mμ.
B. Do p_H 5.3, 440mμ.
C. Fe^{3+}-Reagent, p_H 5.30, 440 mμ.

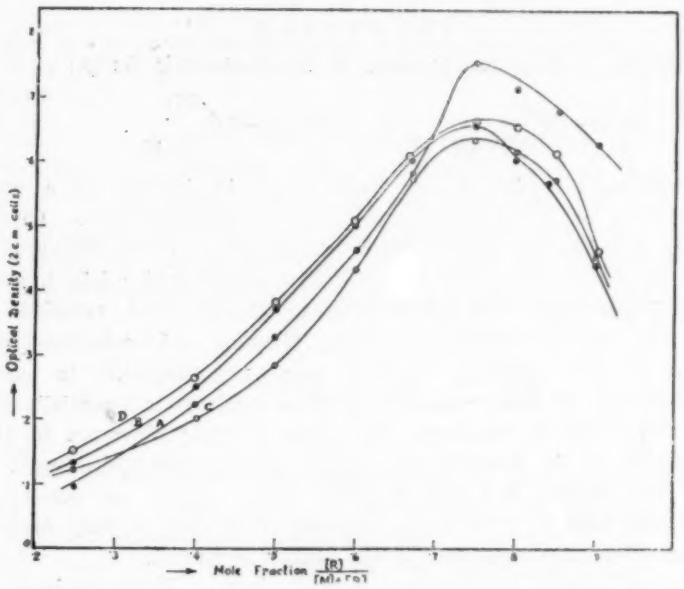
In another set 0.002 *M* ferric iron and 0.002 *M* reagent solutions were mixed (metal + reagent = 20 c.c.). To each of these solutions was added 20 c.c. of a sodium acetate-HCl buffer of p_H 5.3, the solutions made up to 50 c.c. and optical densities were read at 440 mμ and also at 500 mμ in 2 cm cells. At 440 mμ the iron solutions at p_H 5.3 had some absorption, but only very negligible absorption at 500 mμ. The absorption of iron under these conditions was determined separately and corrections for these absorptions made. The corrected optical densities were plotted against mole fraction of the reagent. The curves at 440 mμ and also at 500 mμ (not shown in Fig. 5) show a maximum at 0.75, indicating an 1 : 3 complex between ferric iron and the reagent (curve B, Fig. 5).

A similar determination was also made with 0.002*M* ferrous ammonium sulphate and 0.002*M* reagent solution at p_H 5.3. Here, however, in presence of acetate buffer the colour development was slow, and therefore the optical density measurements were taken after 2½ hours at 440 mμ and also at 500 mμ in 2 cm

cells. The ferrous solutions under these conditions had negligible absorption. Maximum in the optical density-mole fraction curve again occurs at 0.75, indicating an 1 : 3 complex (curve C, Fig. 5).

Fig. 6

Job's curves of vanadium nicotinohydroxamate.



A. 1 : 1 Alcoholic vanadium and 1 : 1 alcoholic reagent, p_H 3.0, 440 mμ.

B. Do p_H 8.5, 500 mμ.

C. Aqueous vanadium and aqueous reagent, p_H 8.0, 500 mμ.

D. Do p_H 3.0, 500 mμ.

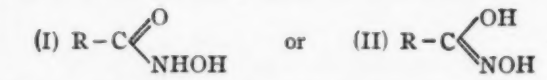
B. Vanadium Colours.—Aqueous equimolar (0.005 *M*) solutions of vanadate and reagent were mixed (metal + reagent = 40 c.c.), p_H adjusted to 3.0, the volume finally made up to 50 c.c. and the optical densities were read at 500 mμ and also at 550 mμ in 2 cm cells. Optical density-mole fraction curve shows an 1 : 3 complex. A similar measurement at p_H 8 gave the maximum in the Job's curve at 0.75, indicating the formation of an 1 : 3 complex (curves C and D, Fig. 6).

1 : 1 Alcoholic vanadium solutions (0.0025 *M*) and 1 : 1 alcoholic reagent solutions (0.0025 *M*) were mixed, keeping the total volume at 40 c.c ; p_H was adjusted to 3 and the volume finally made up to 50 c.c. and optical densities measured at 440 mμ and also at 500 mμ. At 440 mμ, correction for absorption of vanadium was made. Job's curve shows the maximum at 1 : 3 ratio. A similar measurement at p_H 8 with 0.005 *M* solutions at 500 mμ and at 550 mμ indicates an 1 : 3 complex (curves A and B, Fig. 6).

C. Molybdenum Colours.—Molybdenum solution (0.005*M*) and the reagent solution (0.005 *M*) were mixed, keeping the total volume at 40 c.c. p_H was adjusted to 7, volume made up to 50 c.c. and then optical densities measured in 1 cm cells at 400 mμ and at 420 mμ. Job's curves show a peak at 0.67, indicating an 1 : 2 complex (curves A & B, Fig. 3). The molybdenum solutions under the same conditions showed negligible absorption at 400 mμ and at 420 mμ.

Discussion

The hydroxamic acids generally exist in two tautomeric forms:



(I) has one replaceable hydrogen so that it would behave as a monobasic acid. The carbonyl oxygen may function as the co-ordinating source. On the other hand, structure (II) has two replaceable hydrogens, one, of the hydroxyl group and the other, of the oxime group, so that the hydroxamic acid might behave as a dibasic acid. Experiments with pyridinohydroxamic acids have revealed a close similarity in their reaction towards metal ions. Nicotino and *iso*nicotino-hydroxamic acids give rise to the intensely coloured manganic complexes in ammoniacal medium. The nature of iron complexes of these reagents is essentially the same. In their behaviour towards vanadium they reveal a slight difference in that the addition of alcohol to the brown-purple vanadium *iso*nicotinohydroxamate in acid medium, does not produce that intense golden yellow colour as developed with nicotinohydroxamic acid in 50% alcoholic medium. Instead, a dirty brown-yellow colour (with no absorption maximum in the visible) is formed.

Their reaction towards molybdenum is also similar. Picolinohydroxamic acid gives only a weakly coloured manganic complex, develops the usual violet ferric complex and in weak-acid solution gives a precipitate. This reagent exhibits the intense golden yellow vanadium colour in presence of alcohol in acid medium. Its behaviour towards molybdenum is also similar to those of nicotino- and *iso*-nicotino-hydroxamic acids.

These similarities suggest that the reactions shown by these reagents are probably entirely those of the hydroxamic acid groups and possibly the heterocyclic nitrogen does merely influence the solubilities of the metal complexes.

The nature and the analytical aspects of the colour reactions of iron (ferric and ferrous), vanadium and molybdenum with picolino- and *iso*nicotino-hydroxamic acids will form the subject matter of a subsequent communication.

Author's grateful thanks are due to Prof. P. Rây and to Dr. P. C. Banerjee for their valuable advice and good wishes. Thanks are also due to the Ministry of Education, Government of India, for the award of a senior research scholarship, which enabled the author to undertake this investigation.

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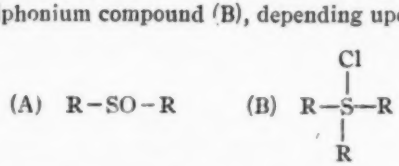
SULPHINATION. PART I. SULPHINATION OF SOME 7-HYDROXYCOUMARIN DERIVATIVES

By R. N. Usgaonkar and G. V. Jadhav*

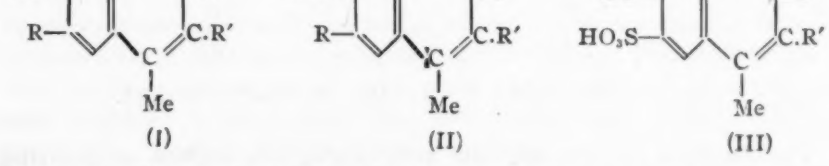
The action of thionyl chloride on some 7-hydroxycoumarin derivatives in presence of anhydrous aluminium chloride has been studied. The reaction has led to the formation of sulphinic acids of the coumarin derivatives.

The action of thionyl chloride on phenols, phenolic ethers and aromatic hydrocarbons in presence of anhydrous aluminium chloride has been studied by various workers (Colby and McLoughlin, *Ber.*, 1887, **20**, 195; Parker, *ibid.*, 1890, **23**, 1884; Michaelis and Loth, *ibid.*, 1894, **27**, 2540; Smiles *et al.*, *J. Chem. Soc.*, 1906, **89**, 696; 1907, **91**, 1118; 1908, **93**, 735; 1910, **97**, 2248) furnishing either sulphoxide (A) or trisulphonium compound (B), depending upon the conditions used.



There is only one instance in literature, that is of *m*-5-xylenol methyl ether, where together with sulphoxide a small quantity of sulphinic acid is also formed (Smiles and Rossignol, *Ber.*, 1908, **93**, 745).

In the present investigation, this reaction has been applied to 7-hydroxy-4-methyl-, 7-hydroxy-3:4-dimethyl- and 7-hydroxy-6 ethyl-4-methyl-coumarins, yielding the respective sulphinic acids (IA), (IB) and (IC) in good yields. They were characterised by preparing ammonium salt and *S*-benzyl*iso*thiourea derivatives.



[A: R=H; R′=H. B: R=H; R′=Me. C: R=Et; R′=H].

The constitution of these sulphinic acids follows from the fact, that they exhibit coloration with alcoholic ferric chloride, indicating $-SO_2H$ group to be in position *ortho* to OH group. In the case of the first two coumarin derivatives, both the positions *ortho* to OH, viz., 6 and 8, are available for the reaction, but

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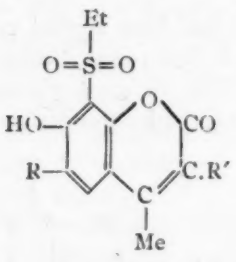
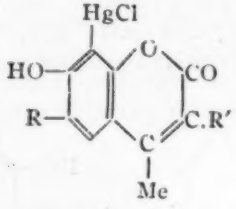
the sulphinic acids obtained from these coumarin derivatives, on oxidation with hydrogen peroxide, give the respective sulphonic acids which are not the same as the known 4-methyl-7-hydroxycoumarin-6-sulphonic acid (IIIA) and 3:4-dimethyl-7-hydroxycoumarin-6-sulphonic acid (IIIB), described by Merchant and Shah (this *Journal*, 1947, **34**, 35; *J. Org. Chem.*, 1957, **22**, 884); hence $-SO_2H$ group must have entered the position '8' of the coumarin derivative, forming (IA) and (IB) respectively. In the case of 4-methyl-6-ethyl-7-hydroxycoumarin, position '6' is already blocked and the only position, *ortho* to OH, available for the reaction is '8'. This has been confirmed as the sulphinic acid, obtained from this coumarin, on oxidation with hydrogen peroxide affords the sulphonic acid (IIC), which has been identified by the mixed m.p. of its *S*-benzyl*iso*thiourea derivative with that of sulphonic acid (IIC), prepared according to Merchant and Shah (*loc. cit.*).

The isolation of the sulphinic acids in a pure state presented difficulties due to their unstable nature. In certain cases the product decomposed during crystallisation, and other methods had to be used to obtain sulphinic acids in pure form (vide Experimental). The sulphinic acids are soluble in alcohol, acetone but insoluble in solvents like benzene, ether etc.

The potassium salts of the sulphinic acids, (IA, IB and IC), on refluxing with alcoholic solution of ethyl iodide furnished the respective ethyl sulphones, (IVA, IVB and IVC), and on treating the sulphinic acids with mercuric chloride, the corresponding chloromercuri derivatives, (VA, VB and VC), were obtained, $-SO_2H$ group being replaced by -HgCl radical.



(IV)



(V)

[A: R=H; R′=H. B: R=H; R′=Me. C: R=Et; R′=H].

The formation of the sulphinic acids during the reaction is interesting, and this provides a new and direct method for the synthesis of sulphinic acids of hydroxycoumarin derivatives, which otherwise would have been difficult to obtain. The amount of anhydrous aluminium chloride used in this reaction is three moles to one mole of coumarin as recommended in the Fries and Friedel-Crafts reactions of the coumarin derivatives (Thakor and Shah, this *Journal*, 1946, **23**, 199). Thionyl chloride was used in a little excess as poor yields were obtained by using theoretical quantity.

EXPERIMENTAL

4-Methyl-7-hydroxycoumarin-8-sulphinic Acid (IA).—Thionyl chloride (6.4 g., 2*M*) was gradually added to an intimate mixture of 4-methyl-7-hydroxycoumarin (5 g., 1*M*) and powdered anhydrous $AlCl_3$ (11.3 g., 3*M*), cooled in ice. The reaction mixture, which turned into a transparent mass, was left overnight at room temperature. Crushed ice and HCl (24 c.c.) were added to the mixture when the milky solution slowly deposited a crystalline solid after scratching the walls of the container and leaving it in a refrigerator overnight. The impure solid was filtered, washed and dried in vacuum. It was then triturated with sodium bicarbonate solution (dilute ammonium hydroxide may also be used) and filtered from the insoluble residue comprising mainly unchanged coumarin and other impurities. The filtrate was made just neutral and any flocculent precipitate separating was removed and to the clear solution more HCl added, scratched and left in the refrigerator. White sulphinic acid slowly separated. It was filtered, washed and dried in vacuum. M.p. varied from 155-65° (decomp.), yield 3-4 g. The substance on crystallisation from alcohol melted at a lower temperature than the crude one. The pure sample of sulphinic acid was therefore obtained by acidifying its ammonium salt (*vide infra*), m.p. 175-77° (decomp.). (Found: S, 13.50. $C_{10}H_8O_5S$ requires S, 13.33%). It gave a deep purple coloration with alcoholic ferric chloride and no fluorescence with alkali.

Ammonium Salt.—Dry ammonia gas was bubbled in ice-cooled solution of the sulphinic acid (IA, 0.5 g.) in absolute alcohol (5 c.c.) till saturation. Ammonium salt separated slowly in a crystalline form. It was crystallised from alcohol containing a few drops of water in shining needles, m.p. 205-207° (decomp.). (Found: N, 5.76. $C_{10}H_{11}O_5NS$ requires N, 5.45%). It is very soluble in water.

S-Benzylisothiourea Derivative.—Potassium salt of the sulphinic acid (IA) was first prepared by adding alcoholic potash dropwise to the alcoholic solution of the sulphinic acid with good stirring till permanent yellow tinge appeared in the solution. The white salt separating was filtered, washed well with alcohol and dried in vacuum.

To the aqueous solution of the potassium salt a saturated aqueous solution of *S*-benzylisothiourea hydrochloride (Chamber and Watts, *J. Org. Chem.*, 1941, **6**, 376) was added at room temperature when a yellowish oil separated which gradually solidified. It crystallised from 25% alcohol, m.p. 121-23° (decomp.). (Found: N, 6.89. $C_{18}H_{18}O_5N_2S_2$ requires N, 6.89%).

The above derivative was also prepared directly by adding dropwise NaOH solution to sulphinic acid, suspended in water, till a yellow tinge appeared in the solution. The yellow tinge was destroyed by adding a little more of sulphinic acid, the excess of which was filtered off, and to the filtrate an aqueous solution of *S*-benzylisothiourea hydrochloride was added. The product was isolated as before.

4-Methyl-7-hydroxycoumarin-8-sulphonic Acid (IIA): (*Sodium salt*).—Hydrogen peroxide (3 c.c. of 100 vol. + 7 c.c. of water) was added to the solution of the

above sulphinic acid (0.5 g.) in sodium bicarbonate solution and the reaction was allowed to proceed for about an hour at room temperature and then it was heated on a water-bath for about an hour, cooled, just acidified with HCl, concentrated to a small bulk and poured in a saturated solution of common salt and kept in a refrigerator. The white sodium salt of sulphonic acid which separated was filtered, washed and dried.

S-*Benzylisothiourea* derivative of (IIA), prepared from the above sodium salt, was crystallised from water containing a few drops of alcohol in shining needles, m.p. 195-97°. (Found: N, 6.95. $C_{18}H_{18}O_6N_2S_2$ requires N, 6.64%). The mixed m.p. with the same derivative of 4-methyl-7-hydroxycoumarin-6-sulphonic acid (IIIA), prepared according to Merchant and Shah (*loc. cit.*), gave a depression of about 25°.

4-Methyl-7-hydroxycoumarin-8-ethylsulphone (IVA).—Ethyl iodide (0.5 c.c.) was added to the solution of potassium salt of sulphinic acid (0.5 g.) in a mixture of water (3 c.c.) and alcohol (4 c.c.) and the mixture was refluxed for about 15 hours. A negligible amount of a solid, m.p. 285° (decomp.) (not investigated), which separated from the boiling mixture, was removed and the solution was cooled when the sulphone slowly separated in quite a pure state. It crystallised from alcohol in white flat needles, m.p. 179-80°. (Found: S, 12.20 $C_{12}H_{12}O_5S$ requires S, 11.94%). It is insoluble in water and sparingly soluble in alcohol.

4-Methyl-7-hydroxy-8-chloromercuri-coumarin (VA).—An alcoholic solution of mercuric chloride (1 g.) was added to the sulphinic acid (IA, 0.5 g.) in alcohol (5 c.c.) when a crystalline solid slowly separated with continuous evolution of SO_2. The substance was purified by refluxing first with water and then with alcohol. It did not melt till 270° but became yellowish at 250° and pasty at 270°. (Found: Hg, 49.09. $C_{10}H_7O_3ClHg$ requires Hg, 48.79%). It is insoluble in water and in organic solvents. It dissolves in sodium hydroxide solution with a blue fluorescence.

3:4-Dimethyl-7-hydroxycoumarin-8-sulphinic Acid (IB).—Thionyl chloride (6.4 g.) was added to an intimate mixture of 3:4-dimethyl-7-hydroxycoumarin (5 g.) and anhydrous aluminium chloride (10 g.) and the reaction was allowed to proceed in the same manner as in case of (IA) and worked up similarly. The sulphinic acid was isolated in nearly pure state by following the same procedure, as before. A large amount of mud-like byproducts was removed during the process. It was dried in vacuum (yield 2.5-3 g., m.p. 164-65°, decomp.). It was crystallised from alcohol in needles, m.p. 169-70° (decomp.). (Found: S, 12.35. $C_{11}H_{10}O_5S$ requires S, 12.6%). It developed a blue coloration with alcoholic ferric chloride and no fluorescence with alkali.

Ammonium salt was prepared and crystallised, as before, in shining white prismatic needles, m.p. 205-207° (decomp.). (Found: N, 5.52. $C_{11}H_{13}O_5NS$ requires N, 5.16%). It is very soluble in water and insoluble in alcohol and in other solvents. It gives a bluish violet coloration with alcoholic ferric chloride.

S-*Benzylisothiourea* derivative of (IB), prepared as before, was crystallised from rectified spirit in glistening needles, m.p. 185-87° (decomp.). (Found: N, 6.69. $C_{19}H_{20}O_5N_2S_2$ requires N, 6.66%).

3 : 4-*Dimethyl-7-hydroxycoumarin-8-sulphonic acid* (IIB) was obtained by oxidation of the sulphinic acid in the same way as in (IA) and the sodium salt of sulphonic acid was isolated.

S-*Benzylisothiourea* derivative of (IIB) was prepared from the sodium salt and crystallised from dilute alcohol in monoclinic needles, m.p. 185-87°. (Found : N, 6.85. $C_{19}H_{20}O_6N_2S_2$ requires N, 6.43%). [The m.p. of *S*-benzyl*iso*thiourea derivative of 3 : 4-dimethyl-7-hydroxycoumarin 6-sulphonic acid described by Merchant and Shah (*loc. cit.*) is 224-25°].

3 : 4-*Dimethyl-7-hydroxycoumarin-8-ethylsulphone* (IVB) was prepared by refluxing the solution of potassium salt of sulphinic acid (IB, 1 g.) in a mixture of alcohol (8 c.c.), water (6 c.c.) and ethyl iodide (1.5 c.c.) for 15 hours. The sulphone was crystallised from alcohol in shining plates, m.p. 207-208°. (Found : S-11.67. $C_{13}H_{14}O_5S$ requires S, 11.34%).

3 : 4-*Dimethyl-7-hydroxy-8-chloromercuri-coumarin* (VB) was prepared by adding an alcoholic solution of $HgCl_2$ to an alcoholic solution of sulphinic acid (IB) and was purified as in the case of (VA) in shining needles. It did not melt till 270° but became pasty at this temperature. (Found : Hg, 47.6. $C_{11}H_9O_5ClHg$ requires Hg, 47.2%).

4-*Methyl-6-ethyl-7-hydroxycoumarin-8-sulphinic Acid* (IC).—Thionyl chloride (3.7 c.c. was added to the intimate mixture of 4-methyl-6-ethyl-7-hydroxycoumarin (5 g.) and powdered anhydrous $AlCl_3$ (10 g.) and the reaction was allowed to proceed as in the previous case. The product was worked up similarly, m.p. 160° (decomp.), yield 3-4 g.

This sulphinic acid was found to form insoluble sodium or ammonium salt when treated with sodium bicarbonate or ammonia solution. So the residue obtained after treatment of the crude product with sodium bicarbonate solution was heated to boiling with water and filtered immediately. From the filtrate by acidification with HCl, a good amount of the sulphinic acid was recovered. It was carefully crystallised from dilute alcohol (1 : 1) as small square plates, m.p. 165-67° (decomp.). (Found : S, 11.60. $C_{12}H_{12}O_5S$ requires S, 11.94%).

Ammonium salt of (IC) was prepared and crystallised as usual in glistening needles, m.p. 213-25° (decomp.). (Found : N, 4.91. $C_{12}H_{13}O_5NS$ requires N, 4.90%). It is soluble in hot water.

S-*Benzylisothiourea* derivative of (IC) was prepared from the potassium salt of (IC) and crystallised from dilute alcohol in clusters of needles, m.p. 167-68° (decomp.). (Found : S, 6.25. $C_{20}H_{22}O_5N_2S_2$ requires S, 6.45%).

4-*Methyl-6-ethyl-7-hydroxycoumarin-8-sulphonic Acid* (IIC).—The oxidation was carried out in acetic acid medium, by adding hydrogen peroxide (6 c.c. of 100 vol. + 14 c.c. of water) to the suspension of the sulphinic acid (IC, 1 g.) in acetic acid (5 c.c.) with good shaking at room temperature. Sulphinic acid went into solution within 15 minutes. It was then diluted with water (20 c.c.) and left overnight and then neutralised with NaOH solution, when sodium salt of sulphonic acid separated, the separation being facilitated by adding sodium chloride. It was filtered, washed and dried.

S-*Benzylisothiourea* derivative of (IIC), prepared from the above sodium salt, was crystallised from dilute alcohol in clusters of needles, m.p. 161-62°. Mixed m.p. with the authentic specimen, prepared according to Merchant and Shah (*loc. cit.*), showed no lowering.

4-*Methyl*-6-*ethylcoumarin*-8-*ethylsulphone* (IVC).—Potassium salt of the sulphinic acid (IC) was first dissolved in water (10 c.c.) by heating and it was then refluxed by adding alcohol (12 c.c.) and ethyl iodide (1.5 c.c.) for 16 hours. A small amount of a solid, m.p. 255° (decomp.), that separated from the boiling mixture was removed (not investigated), and the mixture was cooled when the sulphone was obtained in a pure state. It crystallised from alcohol in shining rectangular plates, m.p. 125-27°, yield 0.8 g. (Found: S, 10.37. $C_{14}H_{16}O_5S$ requires S, 10.81%).

4-*Methyl*-6-*ethyl*-7-*hydroxy*-8-*chloromercuri-coumarin* (VC) was prepared from (IC) by adding an alcoholic solution of mercuric chloride and purified as usual as shining needles. It became pasty at 270° (turned yellow at 250°). (Found: Hg, 45.81. $C_{12}H_{11}O_3ClHg$ requires Hg, 45.67%).

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A NEW SERIES OF SALTS OF HEXAFLUOFERRIATES

By Grihapati Mitra

A series of compounds of the general formula $M'M''FeF_6, 6H_2O$ (where M'=K, NH_4, Tl, etc. and M''=Cu, Ni, Zn, etc.) has been described. The corresponding sodium salts crystallise with four or two molecules of water. The method adopted for the preparation of the corresponding hexafluoaluminates has been followed for the isolation of these compounds. The sodium salts are highly soluble. The other compounds are also fairly soluble in water. At high temperature or in absence of water, the $[FeF_6]^{3-}$ ion in these compounds seems to break down. These compounds are isomorphous with the corresponding series of hexafluoaluminates, described previously.

In a previous communication several new compounds of hexafluoaluminates were described (this *Journal*, 1956, **33**, 732). The corresponding compounds of the hexafluoferriate ion are being discussed in the present paper.

Trivalent iron like aluminium gives rise to a series of complex anions with fluorine. The chief amongst these are $[FeF_4]^-$, $[FeF_5]^{2-}$ and $[FeF_6]^{3-}$. Remy and Busch (*Ber.*, 1933, **66B**, 961) have made a systematic study of these fluoride complexes of iron and they have shown that the number of compounds isolated and their stabilities depend upon the formation energies of the Fe—F linkages in different groups. The $[FeF_5]^{2-}$ group from this point of view is the most stable one and most of the salts of the complex fluoride ions of iron belong to this group.

Trivalent iron, however, bears a close resemblance to aluminium, and in the latter case, the hexafluoride complexes are more numerous. The present investigation has shown that by suitable choice of the cation, quite a good number of salts of hexafluoferriate anion can be isolated, and in fact, the number of compounds formed by the hexafluoferriate ion now exceeds those formed by the pentafluoferriate ion.

The following series of compounds have been isolated: $M'M'' FeF_6, 6H_2O$ where M''=Ni, Zn, Cd, Cu etc., and M'=K, Rb, Cu, Tl, NH_4 etc.

The corresponding sodium salts in keeping with the schoenite series and the salts of the corresponding hexafluoaluminate ion, crystallise with four or two molecules of water.

Only a few salts of hexafluoferriate ion were known previously and most, if not all, of them were concerned with the alkali metals. This new series shows an analogy between trivalent iron and aluminium and also offers some scope for the structural study of the hexafluoferriate ion in greater details.

Experimental

Fluorine in the compounds was determined by fusing an weighed amount of the substance with an excess of sodium carbonate for some time and leaching out the resulting mass with water and filtering the leachate. The amount of fluoride ion in solution was determined as calcium fluoride or lead chlorofluoride. The other constituents in the compounds were determined after removing the fluoride ions completely by heating with sulphuric acid.

Methods of Preparation.—The same methods adopted for the preparation of the corresponding hexafluoaluminates were followed (*loc. cit.*). Freshly precipitated ferric hydroxide was dissolved in 20% hydrofluoric acid, heated in a platinum basin on a water-bath. A slight excess over the equimolecular proportion of the bivalent metal (e.g., Cu, Zn, Cd, Ni, etc.) in the form of hydroxide, carbonate or basic carbonate was then added to it. A concentrated solution of alkali metal fluoride or bifluoride was added to the solution with constant stirring. On account of the sparing solubility of sodium fluoride in water, a concentrated solution of sodium carbonate was added to the sodium compounds, followed by the addition of an excess of hydrofluoric acid. The solution was filtered and allowed to concentrate at about 80°. When sufficiently concentrated, these were kept in a vacuum desiccator (conc. H_2SO_4). The sparingly soluble alkali metal hexafluoroferriates tend to precipitate down easily. Hence, from time to time the solution was filtered and allowed to crystallise once more. After a few days beautiful crystals appeared. All the compounds belonging to this series formed beautiful crystals; the alkali metal hexafluoferriates, on the other hand, precipitated down as powder. These beautiful crystals, sometimes coloured, could easily be distinguished when they started to appear at the bottom of the solution. A lower temperature (below 10°) was found to favour the formation of the sodium compounds. At higher temperatures Na_3FeF_6 precipitated down very easily. A slight excess of hydrofluoric acid seemed to favour the formation of these compounds. The following compounds were isolated.

Sodium copper hexafluoferriate dihydrate.—(Found: Fe, 18.96; Cu, 21.53; F, 38.78. $NaCuFeF_6$, $2H_2O$ requires Fe, 19.10; Cu, 21.76; F, 38.98%).

Potassium copper hexafluoferriate hexahydrate.—(Found: Cu, 16.63; Fe, 14.53; F, 29.82. $KCuFeF_6$, $6H_2O$ requires Cu, 16.70, Fe, 14.67; F, 29.95%).

Ammonium copper hexafluoferriate hexahydrate.—(Found: NH_4, 5.03; Cu, 17.45; Fe, 15.31; F, 31.36. NH_4CuFeF_6, $6H_2O$ requires NH_4, 5.02; Cu, 17.68; Fe, 15.53; F, 31.71%).

Rubidium copper hexafluoferriate hexahydrate.—(Found: Rb, 19.43; Cu, 14.81; Fe, 12.91; F, 26.42. $RbCuFeF_6$, $6H_2O$ requires Rb, 20.03; Cu, 14.89; Fe, 13.08; F, 26.70%).

Thallium copper hexafluoferriate hexahydrate.—(Found: Tl, 37.16; Fe, 10.11; Cu, 11.33; F, 20.58. $TlFeF_6$, $6H_2O$ requires Tl, 37.44; Fe, 10.23; Cu, 11.64; F, 20.88%).

Ammonium zinc hexafluoferriate hexahydrate.—(Found: NH_4, 4.77; Zn, 17.86; Fe, 15.28; F, 31.31. NH_4ZnFeF_6, $6H_2O$ requires NH_4, 4.99; Zn, 18.09; Fe, 15.45; F, 31.55%).

Potassium zinc hexafluoferriate hexahydrate.—(Found : Zn, 16.78 ; Fe, 14.32 ; F, 29.36. $KZnFeF_6$, $6H_2O$ requires Zn, 17.09 ; Fe, 14.59 ; F, 29.81%). Loss in wt. at 110°, 27.89 ; calc. for the anhydrous compound, 28.26.

Sodium zinc hexafluoferriate tetrahydrate.—(Found : Zn, 19.38 ; Fe, 16.78 ; F, 34.18. $NaZnFeF_6$,$4H_2O$ requires Zn, 19.79 ; Fe, 16.91 ; F, 34.52. Loss in wt. at 110°, 21.03 ; calc. for the anhydrous compound, 21.81.

Rubidium zinc hexafluoferriate hexahydrate.—(Found : Zn, 15.07 ; Rb, 19.73 ; Fe, 12.81 ; F, 26.50. $RbZnFeF_6$,$6H_2O$ requires Zn, 15.24 ; Rb, 19.94 ; Fe, 13.03 ; F 26.59%).

Ammonium cadmium hexafluoferriate hexahydrate.—(Found : Cd, 27.31 ; Fe, 13.26 ; NH_3, 3.92 ; F, 13.40. NH_4CdFeF_6, $6H_2O$ requires Cd, 27.52 ; Fe, 13.67 ; NH_3, 4.17 ; F, 13.65%).

Thallium cadmium hexafluoferriate hexahydrate.—(Found : Cd, 18.58 ; Tl, 34.13 ; Fe, 9.21 ; F, 18.82 $TlCdFeF_6$, $6H_2O$ requires Cd, 18.89 ; Tl, 34.36 ; Fe, 9.39 ; F, 19.17%).

Rubidium cadmium hexafluoferriate hexahydrate.—(Found : Cd, 23.18 ; Fe, 11.52 ; Rb, 17.39 ; F, 23.46. $RbCdFeF_6$,$6H_2O$ requires Cd, 23.62 ; Fe, 11.74 ; Rb, 17.97 ; F, 23.96%).

Sodium nickel hexafluoferriate tetrahydrate.—(Found : Ni, 18.07 ; Fe, 16.98 ; F, 34.91. $NaNiFeF_6$, $4H_2O$ requires Ni, 18.13 ; Fe 17.26 ; F, 35 23%).

Ammonium nickel hexafluoferriate hexahydrate.—(Found : Fe, 15.15 ; Ni, 16 41 ; NH_4, 4.92 ; F. 31.88. NH_4NiFeF_6, $6H_2O$ requires Fe, 15.74 ; Ni, 16.55 ; NH_4, 5.09 ; F, 32.14%).

Thallium nickel hexafluoferriate hexahydrate.—(Found : Ni, 10.62 ; Tl, 37.48 ; Fe, 10.08 ; F, 20.66. $TlNiFeF_6$, $6H_2O$ requires Ni, 10.85 ; Tl, 37.78 ; Fe, 10.33 ; F, 21.08%).

General Properties.—These compounds are crystalline and stable under ordinary conditions and turn brown slowly in moist air, due evidently to the formation of ferric hydroxide. These compounds, when left in dry air for weeks, slowly lose water molecules and are transformed to white powders which remain insoluble in water. The compounds lose water rapidly at higher temperature (100°) and are converted to a mixture of metallic fluorides and insoluble fluoferriates of the alkali metals.

Methods of Analysis.—After removal of fluorine by heating the salts with concentrated sulphuric acid, the metals were estimated by following the standard methods of analysis. For the estimation of fluorine, the compounds were fused with sodium carbonate and from the solution fluorine was determined gravimetrically as calcium fluoride.

The sodium salts are highly soluble in water. All the crystalline compounds can be recrystallised from water. In each time, however, some amount of the insoluble alkali metal fluoferriates is precipitated at first.

The crystalline overgrowth of NH_4ZnAlF_6, $6H_2O$ on NH_4CuFeF_6, $6H_2O$ has been observed.

The nature of link between the fluorine atoms of $[FeF_6]^{3-}$ group and the divalent metals has been discussed in the previous paper in connection with the hexafluoaluminates.

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CHEMISTRY OF BERYLLIUM. PART IV. NORMAL ORGANIC SALTS OF BERYLLIUM

By Sarju Prasad and Kashi Prasad Srivastava

The normal beryllium salts of lauric, myristic, palmitic, stearic, sebacic, malic, citric, benzoic, salicylic and phthalic acids have been prepared and their properties studied.

Extensive work has been done on the formation of organic salts of beryllium by saturating aqueous solution of organic acids with beryllium carbonate or hydroxide (Parson, "The Chemistry and Literature of Beryllium"; Steinmetz, *Z. anorg. Chem.*, 1907, **54**, 217; Tantar and Kurowski, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 936; *J. Chem. Soc.*, 1907, **94**, 166; Glassmann, *Chem. Ztg.*, 1907, **31**, 8; Tantar, *Ber.*, 1910, **43**, 1230). According to Parson (*J. Phys. Chem.*, 1907, **11**, 659) salts obtained by this method are only solid solutions.

Bury *et al.* (*ibid.*, 1930, **34**, 563) prepared beryllium salicylate [$Be(C_6H_4O.CO_2)2H_2O$] which according to him existed in a dimeric form, *i.e.*, $Be(Be\ Sal_2)4H_2O$. Funk and Römer (*Z. anorg. allgem. Chem.*, 1938, **239**, 288) obtained beryllium formate and acetate by the interaction of acids and beryllium chloride. Feild (*J. Amer. Chem. Soc.*, 1939, **61**, 1817) prepared a number of normal organic salts of beryllium by heating beryllium chloride and acid in benzene.

From dialysis studies Feldmann *et al.* (*ibid.*, 1951, **73**, 4775) showed that the complex with citric acid was stable below p_H 8.5 and had a constant molar ratio of 1 : 2.

The present investigation was undertaken to study the formation of normal salts of beryllium with mono- and dicarboxylic acids and hydroxy-acids by a general method and the properties of the salts formed.

Experimental

Beryllium chloride was prepared according to Pollok (*J. Chem. Soc.*, 1904, **85**, 603), containing small quantities of carbon and oxide. It was purified by resublimation in an atmosphere of dry nitrogen mixed with dry chlorine. As beryllium chloride is insoluble, but some of the compounds formed are soluble in benzene and others are insoluble in organic solvents, different methods have been adopted for their preparation.

Salts of Beryllium (soluble in benzene).—The acid (~ 4-6 g.) was weighed out accurately in a hard glass test-tube, mixed well with excess of anhydrous beryllium chloride and heated in an oil-bath at a temperature 10-15° higher than the m.p. of the acid. When the evolution of HCl (gas) had ceased (10-12 hrs.), the mass was cooled, extracted with benzene, evaporated to dryness and kept over calcium chloride for about 24 hours and then analysed.

Salts of Beryllium (insoluble in organic solvents).—$BeCl_2$ (~ 2-3 g.) was mixed well with an excess of the acid. The mixture was heated in an oil-bath at a temperature slightly higher than the m.p. of the acid till there was no further evolution of HCl. The heated mass was taken out, cooled and then washed well with ether or other organic solvents till free of the acid. The residue was dried and analysed.

In the case of beryllium phthalate, the chloride was mixed with an excess of phthalic acid and heated in a furnace at 210-15° for about 8-10 hours. The mass was washed well with ether, dried and analysed. In all these cases the reaction was carried out in an inert atmosphere of dry nitrogen.

Analysis of the Compounds.—Weighed quantity of the substance (1-2 g.) was boiled with a mixture of HCl (conc.) and HNO_3 (conc.), cooled, diluted and filtered. The filtrate was treated with NH_4OH (dil.) when beryllium was precipitated as $Be(OH)_2$. It was filtered, washed free of electrolytes with 2% ammonium acetate solution, dried, ignited and weighed as BeO. The percentage of beryllium and the empirical formula of the compound were calclated from the weight of BeO obtained. To check the results, carbon and hydrogen were estimated by combustion method using Heraeus Macro Combustion Furnace in a few cases.

General Properties.—Of all the compounds prepared, only beryllium laurate is a colorless liquid at the room temperature and the rest are solids. It is miscible with benzene, chloroform, carbon tetrachloride, acetone and ether but immiscible with absolute alcohol and mineral acids. Beryllium palmitate and stearate are soluble in benzene, carbon tetrachloride. chloroform but insoluble in ether, whereas beryllium myristate is soluble only in benzene but insoluble in other solvents.

Beryllium sebacate, malate, citrate, benzoate, salicylate and phthalate are insoluble in common organic solvents. Beryllium malate and citrate swell up on heating and do not melt. Beryllium salicylate and phthalate do not melt up to 400°.

TABLE I

Acids.	Beryllium (%). Found.	Calc.	Carbon (%). Found.	Calc.	Hydrogen (%). Found.	Calc.	Colour.	M.P.	Formula.
Lauric	2.19	2.21	...	...	...	...	Colourless	...	$[CH_3(CH_2)_{10}COO]_2Be$
Myristic	1.95	1.94	...	...	...	...	Yellowish	36	$[CH_3(CH_2)_{12}COO]_2Be$
Palmitic	1.74	1.73	...	...	...	...	,,	45	$[CH_3(CH_2)_{14}COO]_2Be$
Stearic	1.54	1.57	75.25	75.13	12.23	12.12	,,	54	$[CH_3(CH_2)_{16}COO]_2Be$
Sebacic	4.32	4.31	57.34	57.42	7.53	7.65	Dark ash	...	$[(CH_2)_8COO.COO]Be$
Malic	9.36	9.34	33.15	33.22	2.01	2.08	Dirty white	...	$[CH_2CHO.(COO)_2]_2Be_3$
Citric	8.77	8.74	...	...	...	...	Dark brown	...	$[(CH_2)_2CO.(COO.)_3]Be_2$
Benzoic	3.56	3.58	...	...	...	...	White	309	$[C_6H_5COO]_2.Be$
Salicylic	6.20	6.21	...	...	...	...	,,	...	$[C_6H_4O.COO]Be$
Phthalic	5.20	5.19	...	...	...	...	Dark ash	...	$[C_6H_4(COO)_2]Be$

DISCUSSION

Beryllium chloride reacts freely with molten mono- and dicarboxylic and hydroxy acids and normal salts are formed. The reaction proceeds with the evolution of HCl till one of the reactants is exhausted.

In the case of monocarboxylic acids, such as lauric, myristic, palmitic, stearic and benzoic acids, one molecule of $BeCl_2$ reacts with two molecules of the acid with formation of the corresponding salt.

With molten sebacic and phthalic acids, which contain two carboxyl groups, the reaction is more vigorous and is completed in a comparatively short time. In this case one molecule of $BeCl_2$ reacts with only one molecule of the acid.

The hydroxy-acids, e. g., malic, citric and salicylic, react vigorously with $BeCl_2$ and the corresponding beryllium salts are formed with evolution of HCl, hydrogen of the hydroxyl and carboxyl groups being displaced in all the cases.

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CHEMISTRY OF BERYLLIUM. PART V. PHENOXIDES OF BERYLLIUM

BY SARJU PRASAD AND KASHI PRASAD SRIVASTAVA

Beryllium phenoxides of α-naphthol, β-naphthol, *o*-cresol, *m*-cresol, catechol, resorcinol, hydroquinone and pyrogallol have been prepared and their constitution discussed. Viscometric studies of the systems $BeCl_2$-β-naphthol-C_2H_5OH, $BeCl_2$-catechol-C_2H_5OH and $BeCl_2$-pyrogallol-C_2H_5OH have also been made.

Fricke and Havestadt (*Z. anorg. Chem.*, 1925, **146**, 121) obtained impure beryllium phenoxide. Funke and Rogler (*ibid.*, 1944, **252**, 323) prepared beryllium phenoxide by the interaction of $BeCl_2$ and phenol, and washing out excess of phenol with carbon tetrachloride. Silber (*Ann. Chim.*, 1952, **7**, 182), however, observed that beryllium phenoxide was readily obtained by the reaction of phenols and beryllium chloride in boiling benzene with the evolution of HCl and separation of the phenoxide.

The present investigation was undertaken with a view to studying the formation of complex compounds of $BeCl_2$ with phenol and the preparation of phenoxides of beryllium with mono-, di- and tri-hydroxyphenols.

EXPERIMENTAL

Beryllium chloride was prepared as reported in Part IV (this *issue*, p. 261).

α-Naphthol, β-naphthol, *o*-cresol, *m*-cresol or resorcinol (double the requisite quantity in each case) was dissolved in benzene and $BeCl_2$ added to it. The content

was heated on a water-bath till the evolution of HCl had ceased. With α- and β-naphthols and *m*-cresol, a compound separated out in each case. With *o*-cresol no product separated ; in this case benzene was distilled off when the residue left behind became insoluble in benzene. The compounds obtained were washed with benzene and dried in vacuum. They were further washed with dry ether, dried and analysed. In the case of resorcinol, a very small quantity of the phenoxide mixed with $BeCl_2$ was obtained.

Resorcinol, catechol, pyrogallol or hydroquinone was dissolved in dry ether and an ethereal solution of $BeCl_2$ was added to it. The mixture was gently warmed on an oil-bath till whole of the ether was evaporated off. The temperature of the oil-bath was then raised 10–20° above the m.p. of the respective phenol, and heating continued till HCl had ceased to evolve. The product obtained in each case was washed repeatedly with dry ether, dried and analysed.

In the case of solid phenols, alternative synthesis was carried out by heating phenols and $BeCl_2$ at a temperature of 10–12° higher than the m.p. of the respective phenol. The reaction took unusually long time for completion (sometime more than 48 hours). In all the cases the reaction was carried out in an atmosphere of dry nitrogen. The compounds obtained in these cases were identical with those obtained in benzene or ether except in the case of α-naphthol, where a compound having an indefinite composition was obtained.

General Properties.—All the compounds are coloured (except *o*-cresoxide which is white). They are insoluble in water and in common organic solvents. They decompose when treated with dilute acids and alkalies. Beryllium resorcinoxide is soluble in dilute NH_4OH and NaOH ; from the former, the compound may be recovered undecomposed.

The compounds were analysed by methods described in Part IV (*loc. cit.*). In a few cases carbon and hydrogen were estimated.

TABLE I

Phenols.	% Beryllium.		% Carbon.		% Hydrogen.		Colour.
	Found.	Calc.	Found.	Calc.	Found.	Calc.	
α-Naphthol	3.07	3.05	...	...	...	...	Dark brown
β-Naphthol	3.08	3.05	...	...	...	...	Ash
o-Cresol	7.72	7.83	73.10	73.04	5.17	5.21	White
m-Cresol	7.79	7.83	73.09	73.04	5.19	5.21	Pink
Catechol	7.70	7.69	...	...	...	...	Black
Resorcinol	7.64	7.69	...	...	...	...	Light brown
Hydroquinone	7.65	7.69	...	...	...	...	Black
Pyrogallol	6.77	6.77	54.00	54.13	3.11	3.00	Black

DISCUSSION

Beryllium chloride forms stable complex compounds with water and alcohol (Fricke and Ruschhaupt, *Z. anorg. Chem.*, 1924, **146**, 103 ; Fricke and Havestadt, *loc. cit.*). The co-ordinate link is through the oxygen atom which acts as the donor.

On mixing ethereal solution of β-naphthol and $BeCl_2$, although no compound separated out, HCl gas evolved slowly which became more pronounced on warming, indicating an interaction between phenol and $BeCl_2$.

Naphthols and cresols react readily with $BeCl_2$ in benzene. Practically the whole of $BeCl_2$ was changed to beryllium phenoxides ; but in the case of resorcinol, a very small quantity of phenoxide mixed with practically the whole of the unchanged $BeCl_2$ was obtained. This is similar to Silber's observation (*loc. cit.*) who found that the solubility of phenol in benzene was responsible for the reaction.

Naphthols and cresols, which are highly soluble in benzene, form phenoxides readily and the reaction proceeds to completion. Resorcinol, which is sparingly soluble, yields only a small quantity of impure phenoxide.

In the case of α- and β-naphthols, two molecules of phenols combine with one molecule of $BeCl_2$ forming the phenoxides, represented as :

$$2C_{10}H_7OH + BeCl_2 \longrightarrow (C_{10}H_7O)_2Be + 2HCl.$$

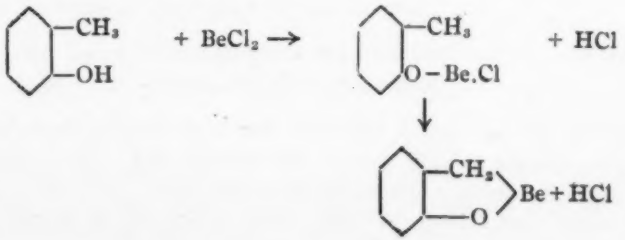
When the reaction is carried out at 10-15° above the m.p. of catechol, resorcinol or hydroquinone, it reacts readily with $BeCl_2$, and pure phenoxide is obtained in each case. In all these cases one molecule of phenol reacts with a molecule of $BeCl_2$ with evolution of HCl.

$$C_6H_4(OH)_2 + BeCl_2 \longrightarrow C_6H_4O_2.Be + 2HCl.$$

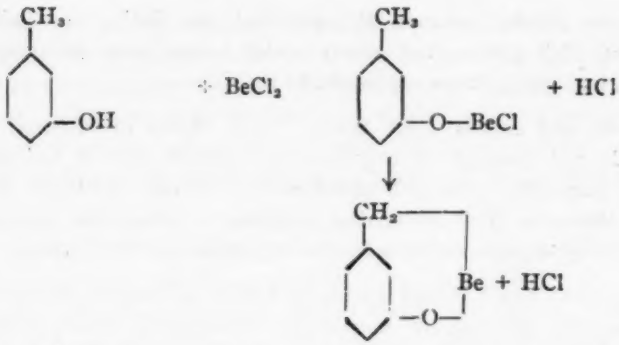
In the case of pyrogallol, only two hydrogen atoms are displaced from the three hydroxyl groups present and the compound is similar to the compounds obtained with dihydroxyphenols. As experiments could not be performed to show which of the two hydrogen atoms takes part in the reaction, no definite structure can be assigned to this compound.

It is interesting to note that one molecule of *o*- or *m*-cresol reacts with one of beryllium chloride although cresols contain only one hydroxyl group. *o*-Cresoxide formed remained dissolved in benzene solution whereas *m*-cresoxide separated out as in the case of α-and β-naphthoxides. From these results it is evident that the methyl group also takes part in the reaction with the ring-closure. It seems probable that the hydroxyl group reacts first with the formation of an intermediate compound ($C_6H_4CH_3O.BeCl_2$) which undergoes orientation and a ring-closure takes place with the evolution of a further molecule of HCl. The reactions can be represented as ;

(*i*)



(ii)



Viscosity of the systems $BeCl_2$—catechol—EtOH, $BeCl_2$—β-naphthol—EtOH and $BeCl_2$-pyrogallol—EtOH was studied, but no indication of the formation of any complex compound was observed in each case.

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CADMIUM SALTS OF ORGANIC ACIDS

By Sarju Prasad, T. Ranganathachar and V. Krishnan

Several salts of cadmium have been prepared by treating an aqueous solution of cadmium chloride with an aqueous solution of the alkali salt of the acid and also by heating anhydrous cadmium chloride with the acid; their properties have been studied and structures discussed.

Pickering (*J. Chem. Soc.*, 1916, **109**, 244) obtained cadmium salts of citric, tartaric and malic acids by mixing aqueous solutions of a soluble cadmium salt and the potassium salt of the acid. Grosmann and Jager (*Z. anorg. Chem.*, 1916, **73**, 48) prepared cadmium acetate-4 ammonia, cadmium formate-3 pyridine, and cadmium formate-1 phenylhydrazine. Dubsky and Tritilek (*Chem. Listy*, 1935, **29**, 76) studied the reaction of aminobenzoic acids with cadmium and zinc salts and found that a solution of the free acid did not react with the cadmium salt, but on addition of sodium acetate only the *ortho*-acid gave a precipitate. In the case of *para*-acid, a basic salt [COOK. $Cd(COONH_2.C_6H_4)_2.2H_2O$] was obtained on neutralisation with KOH. Gebauer (*Z. anorg. Chem.*, 1928, **176**, 283) prepared acetylides, $CdC_2.C_2H_2$, by passing acetylene through a solution of $CdCl_2.NH_2.Ph$ in acetone.

As a very few cadmium salts with organic acids were reported in the literature, the present investigation was undertaken with a view to studying the conditions of preparation and properties of some of them.

Experimental

The acids and cadmium chloride used were of B.D.H. 'Pure' quality.

General Method of Preparation.—The cadmium salts were prepared by two methods.

(*i*) A saturated solution of cadmium chloride was mixed with a concentrated solution of sodium salt of the acid when a precipitate was obtained. It was filtered, washed free of electrolytes and dried in an air-oven.

(*ii*) In this case two series of experiments were carried out; in one case an excess of the acid and in the other, an excess of $CdCl_2$ were used.

A mixture of cadmium chloride and the acid was heated on an oil-bath till the evolution of HCl had ceased. The product was washed free of the acid or $CdCl_2$, as the case may be, and dried. Cadmium was estimated as cadmium sulphate and the organic matter obtained by difference. The same compound was obtained in all the three cases.

TABLE I

Cadmium salts of organic acids.

Acids.	Mol. formula of the Cd salts.	Colour.	M.P.	% Cadmium.		% Organic matter (by diff).	
				Found.	Calc.	Found.	Calc.
Benzoic	$Cd(C_6H_5COO)_2$	White	280°*	28.88	29.08	71.12	70.92
Salicylic	$Cd[C_6H_4(OH)COO]_2$	Pale white	242°*	31.82	31.89	68.18	68.11
Phthalic	$Cd[C_6H_4(COO)_2]$	Greyish white	272°	40.22	40.66	59.78	59.34
Cinnamic	$Cd[C_6H_5CH=CHCOO]_2$	White	260°	27.87	27.66	72.13	72.34
Citric	$\left[\begin{array}{l} CH_2COO \\ \vert \\ C(OH)COO \\ \vert \\ CH_2COO \end{array}\right]_2 Cd_3$	Pale white	153°	46.89	47.15	53.11	52.85
Lauric	$Cd[CH_3(CH_2)_{10}COO]_2$	Milky white	101°	21.10	21.96	78.82	78.04
Myristic	$Cd[CH_3(CH_2)_{12}COO]_2$	White	92°	18.99	19.79	81.01	80.21
Palmitic	$Cd[CH_3(CH_2)_{14}COO]_2$	,,	282°	17.93	18.03	82.07	81.97
Stearic	$Cd[CH_3(CH_2)_{16}COO]_2$	,,	134°	12.98	13.16	87.02	86.84
Maleic	$CdOOC.CH=CH.COOCd$	Ash	260° *	66.01	66.27	33.99	33.73
Tartaric	$CdOOC \quad COOCd$ $\diagdown CH(OH)_2 \diagup$	,,	242°	62.20	62.48	37.80	37.52

*—Decomposed.

From the results it is evident that cadmium behaves consistently as a divalent element and displaces the H of the carboxylic group in the salt formation. No basic salts were obtained in any of the cases studied. In the case of hydroxy-acids, viz., citric, salicylic and tartaric acids, the H of the hydroxyl group was not replaced even when $CdCl_2$ was in excess. The salts are stable in atmosphere, not easily decomposed by dilute acids or by water.

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART I. LEAD MONO-ACETATO COMPLEX

By S. N. Banerjee, A. K. Sen Gupta and S. K. Siddhanta

The composition of the complex formed between Pb^{2+} and acetate ions has been found to be $PbAc^+$ from a study of the equilibrium H^+-ion concentrations in mixtures of equimolecular lead nitrate and acetic acid solutions by "Job's method of continued variation" using a new index property, viz., the increase of H^+-ion concentration.

The thermodynamic dissociation constant, K, for the equilibrium, $PbAc^+ \rightleftharpoons Pb^{2+} + Ac^-$, has been found out as 3.31×10^{-3} at 32.0° – 30.0° by the direct application of "law of mass action", taking into account the activity coefficients of the individual ions, calculated from the ionic strength of the solution mixtures of lead nitrate and acetic acid, employing the "Debye-Hückel limiting law".

Job's method of continued variation (*Compt. rend.*, 1925, **180**, 928; *Ann. chim.*, 1928, *x*, **9**, 113) has been extensively used in determining the composition of a compound A_mB_n formed in aqueous solution between two molecular or ionic entities, 'A' and 'B'. The method, to a less extent, has been applied to find out the dissociation constant of such a compound. In this method, the difference 'Y' between the value of an additive molecular property (e.g. molar extinction, molar conductivity etc.) calculated for any mixture of 'x' c.c. of a solution of 'B' of molar concentration 'pC' and '1-x' c.c. of a solution of 'A' of molar concentration 'C', and the observed value of the property for the mixture is determined. The plot of 'Y' against 'x' here gives a curve with a maximum or a minimum. From the value of 'x' at the maximum or the minimum point, the ratio m/n (*i. e.* composition of the complex) and the dissociation constant 'K' of the complex,

$$\left(K = \frac{A^m B^n}{A_m B_n} \right),$$

are determined using equimolecular ($p = 1$) and non-equimolecular ($p \neq 1$) parent solution respectively.

The method has been described in detail by Siddhanta (this *Journal*, 1948, **25**, 579) and by Martell and Calvin ("Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York, 1952).

Various such additive molar properties were used for this purpose by different workers in the past; e. g., molar extinction coefficient used first by Job (*loc. cit.*) and afterwards by a good number of other workers (vide Martell and Calvin, *loc. cit.*, pp. 29, 34); molar refractivity used by Spacu and Popper (*Bull. Soc. Stiinte*, Cluj, 1934, **7**, 400; 1934, **8**, 5); molar conductivity used first by Purkayastha and Sen Sarma (this *Journal*, 1946, **23**, 31) and subsequently by others; molar heat content by Siddhanta (*loc. cit.*).

In the present work it has been observed that, on mixing lead nitrate and acetic acid solutions, there is a considerable fall in p_H, indicating the liberation of hydrogen ions through a reaction like,

$$m\,Pb^{2+} + n\,HAc \rightleftharpoons (Pb_mAc_n)^{+(2m-n)} + n\,H^+,$$

a complete dissociation for the acid, $H_n(Pb_mAc_n)$ being assumed. There are many such reactions involving complex formation in solution in which the acidity of the medium increases.

In any such case, suppose $[H^+]_A$ is the H^+-ion concentration of $(1-x)$ volume of a solution of 'A' diluted to a volume 1, and $[H^+]_B$ is that of 'x' volume of a solution of 'B' diluted to a volume 1. Now, if $[H^+]_{obs}$ is the hydrogen-ion concentration of the mixture of $(1-x)$ volume of 'A' and 'x' volume of 'B', then the increase in H^+-ion concentration due to complex formation is given by

$$Y = [H^+]_{obs} - \{[H^+]_A + [H^+]_B\}.$$

For the purpose of evaluating 'Y', however, no distinction has been made between '$a_H{}^+$' and $[H^+]$, *i. e.* '$a_H{}^+$', as calculated from the observed p_H of the solution, has been taken equal to $[H^+]$ for every solution.

If the reactant 'A' is a neutral substance like Pb^{2+} ion, and the reactant 'B' be a weak acid like HAc, it is easy to see that the value of 'Y' for any mixture is approximately, though not strictly, proportional to the concentration of the complex A_mB_n. Therefore a plot of 'Y' against 'x' would show a maximum, where $[A_mB_n]$ is maximum. Hence, we propose for such cases that the increase in acidity 'Y' may be used for applying Job's method for the determination of the composition of the complex, using equimolecular parent solutions.

Following such a procedure and employing equimolecular parent solutions of lead nitrate and acetic acid, it has been found in the present work that all the three sets of independent $Y-x$ plots, obtained (Fig. 1), show a maximum value of 'Y' for $x = 0.5$. At this point,

$$m/n = (1-x)/x = 1$$

and the reacting proportion of lead nitrate and acetic acid is 1 : 1. Assuming that lead nitrate and nitric acid undergo complete dissociation, the reaction can therefore be written as

$$Pb^{2+} + HAc \rightleftharpoons [PbAc]^+ + H^+ \qquad \ldots \qquad (A)$$

The complete dissociation of lead nitrate in dilute aqueous solution has already been established by Prasad and Aditya (this *Journal*, 1951, **28**, 683). The maxima in all the three curves are clear and unequivocal, showing that no higher complexes, e.g, $PbAc_2$, $[PbAc_3]^-$, are formed to any appreciable extent under the conditions of the experiment.

In the present work, Job's method for determining the dissociation constant 'K' for the complex $PbAc^+$ has not been used since (*i*) the curve in Job's method as a rule does not show a sharp maximum ; consequently it involves the error in locating the maximum point ; (*ii*) the method is indirect as the maximum point of the curve is to be obtained by intrapolation ; and (*iii*) the proportionality of 'Y' and $[PbAc^+]$ is not rigorously true.

A direct method for determining the thermodynamic dissociation constant of $PbAc^+$ ion, described below, has been used in the present work in preference to Job's method.

In any mixture of lead nitrate and acetic acid in aqueous solution, the existence of the following equilibria are feasible in addition to the one represented by eq. (A).

$$(PbAc)^+ \rightleftharpoons Pb^{2+} + Ac^- \quad \ldots \quad \ldots \quad \ldots \quad (B)$$

$$HAc \rightleftharpoons H^+ + Ac^- \quad \ldots \quad \ldots \quad \ldots \quad (C)$$

The existence of lead diacetate or lead polyacetato ions or polymeric lead acetato complexes is improbable for reasons stated afterwards (vide Discussion), and therefore they need not be considered.

Using symbols with usual meanings, the dissociation constant of $PbAc^+$ ion (eq. B) is given by

$$K = \frac{a_{Pb^{2+}} a_{Ac^-}}{a_{PbAc^+}} = \frac{c_{Pb^{2+}} . c_{Ac^-}}{c_{PbAc^+}} + \frac{f_{Pb^{2+}} . f_{Ac^-}}{f_{PbAc^+}} \quad \ldots \quad \ldots \quad (1)$$

The total acetate entity taken is given by

$$C_a = C_x = c_{PbAc^+} + c_{Ac^-} + c_{HAc} \quad \ldots \quad \ldots \quad (2)$$

The undissociated acetic acid remaining at equilibrium is given by

$$c_{HAc} = C_a - c_{H^+} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Since part of the acetic acid originally added reacts according to (A) and another part dissociates according to (C), and the rest remains undissociated.

If 'K_a' is the ionisation constant of acetic acid (eq. C), we have,

$$c_{Ac^-} = \frac{K_a . c_{HAc}}{c_{H^+} . f_{H^+} . f_{Ac^-}} \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

assuming $f_{HAc} = 1$, HAc being a non-electrolyte. Combining equations (2) and (3), we have

$$c_{PbAc^+} = c_{H^+} - c_{Ac^-} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

Again, $c_{Pb^{2+}}$ = total Pb^{2+} ions originally taken − lead in the complex

$$= C(1-x) - c_{PbAc^+} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

assuming complete dissociation for lead nitrate.

To evaluate the activity coefficients, we need know the ionic strength, 'μ', of the solution given by the expression,

$$\mu = \tfrac{1}{2} (4c_{Pb^{2+}} + c_{PbAc^+} + c_{H^+} + c_{NO_3^-} + c_{Ac^-}) \quad \ldots \quad (7)$$

Then, the activity coefficients can be calculated by applying the "Debye-Hückel limiting law" as shown below:

$$f_{H^+} = f_{Ac^-} = f_{PbAc^+} = f_1 = \text{antilog } (-0.5 \times 1 \sqrt{\mu}) \quad \ldots \quad \ldots \quad (8a)$$

and, $f_{Pb^{2+}} = f_2 = f_1^4 = \text{antilog } (-4 \times 0.5 \times 1 \sqrt{\mu}) \quad \ldots \quad \ldots \quad (8b)$

taking 0.51 to be the Debye-Hückel constant at the temperature of the experiment. For the first approximation, we assume the applicability of the "Debye-Hückel limiting law" to the dilutions used.

From our experimental procedure of determining the p_H of solution mixtures of lead nitrate and acetic acid after attainment of equilibrium, we can know the value of '$a_H{}^+$' at equilibrium. For the purpose of evaluation of 'f_1' and 'f_2' *, we take "$a_H{}^+ = c_H{}^+$" and find 'c_{HAc}' from equation (3); this does not involve a serious error since "$C_a \gg c_H{}^+ > c_H{}^+ - a_H{}^+$". Then, we may find out the value of '$a_{Ac}{}^-$' for knowing '$a_{PbAc}{}^+$' from a modification of equation (5), viz.

$$f_1 c_{PbAc}{}^+ = f_1 c_H{}^+ - f_1 c_{Ac}{}^-$$

$$\text{or} \quad a_{PbAc}{}^+ = a_H{}^+ - a_{Ac}{}^- \qquad \ldots \quad (5a)$$

We then, approximately evaluate '$c_{Pb}{}^{2+}$' by putting "$c_{PbAc}{}^+ = a_{PbAc}{}^+$" in equation (6); this also does not cause a serious error since, "$C(1-x) \gg c_{PbAc}{}^+ > c_{PbAc}{}^+ - a_{PbAc}{}^+$".

Now, we evaluate 'μ' from equation (7) by putting "$c_{Ac}{}^- = a_{Ac}{}^-$", "$c_{PbAc}{}^+ = a_{PbAc}{}^+$" and "$a_H{}^+ = c_H{}^+$", and this also does not cause a large error since,

"$(4c_{Pb}{}^{2+} + c_{NO_3}{}^-) \gg (c_{PbAc}{}^+ + c_H{}^+ + c_{Ac}{}^-) > [(c_{PbAc}{}^+ + c_H{}^+ + c_{Ac}{}^-) - (a_{PbAc}{}^+ + a_H{}^+ + a_{Ac}{}^-)]$"

'$c_{NO_3}{}^-$' is taken equal to '$2C(1-x)$', assuming complete dissociation for lead nitrate.

From this value of 'μ', which is fairly accurate, 'f_1' and 'f_2', are calculated by applying equations (8a) and (8b).

Now, we can put "$c_H{}^+ = \frac{a_H{}^+}{f_1}$" and recalculate a more accurate value of 'c_{HAc}' and hence of '$c_{Ac}{}^-$' from equations (3) and (4) respectively. Using this new value of '$c_{Ac}{}^-$' a more accurate value of '$c_{PbAc}{}^+$' and '$c_{Pb}{}^{2+}$' can be calculated from equations (5) and (6) respectively. Putting the corrected values, thus obtained, in equation (1) in a slightly modified form, viz.,

$$K = \frac{c_{Pb}{}^{2+} . c_{Ac}{}^-}{c_{PbAc}{}^+} . f_2 \qquad \ldots \quad \ldots \quad \ldots \quad (1a)$$

we can calculate the value of 'K'.

* The terms 'activity' and 'activity coefficient' can have a physical significance only in the case of a thermodynamic component. An individual ion cannot be regarded as thermodynamic component, *i. e.* an independently variable constituent, since the amounts of positive and negative ions are interdependent. Hence, the use of 'f_1' and 'f_2' etc. as activity coefficients of individual ion for the purpose of evaluating thermodynamic constant 'K', is theoretically objectionable. We may point out that no theoretical objection can arise, if we regard 'f_1' and' f_2' as multiplication operators rather than definite thermodynamic quantities.

The values of 'K', calculated by such a method in different solution mixtures, are not, however, accurate since they are dependent on the ionic strength of the respective solutions; for though the values of ionic strengths 'μ' are fairly accurate, the values of the activity coefficients 'f_1' and 'f_2', calculated from the 'Debye-Hückel limiting law" are somewhat approximate, the law being inapplicable to solutions with finite ionic strengths. The error in 'K', calculated as above, is therefore greater and greater in cases of solutions with larger and larger ionic strengths; hence, there is a progressive increase in the values of 'K' in Table II with increasing dilution.

The dependence of 'K', so calculated, on the respective ionic strengths of the corresponding solution mixtures is proved clearly by plotting 'K' against 'μ', which process yields one smooth single curve, using data from Table II (vide Fig. 2). This curve, when extrapolated to zero ionic strength, should give the true value of the thermodynamic constant 'K' (when $f_1 = f_2 = 1$). But such an extrapolation may be regarded as objectionable, since the slope of the curve in different regions of the extrapolated portion is unknown. We have, however, found that when pK ($= -\log K$) is plotted against $\sqrt{\mu}$ *, it gives a straight line curve, which satisfies all the experimental data obtained (vide Fig. 3). The extrapolation of this straight line to $\sqrt{\mu} = 0$ is less objectionable, and in this way therefore we can find a very accurate value of 'K'.

EXPERIMENTAL

Exact 0.1 M, 0.2 M and 0.333 M solutions of lead nitrate (E. Merck, Darmstadt) were prepared by direct weighing of the calculated amounts. Acetic acid (Analar) solutions of strengths 0.1 M, 0.2 M and 0.333 M were prepared (standardised against standard caustic soda solution). All solutions and dilutions were made with conductivity water. All solution mixtures shown in the tables were prepared from these parent solutions. The p_H of all solutions was measured at room temperature by a Beckman p_H-meter (type G). It has been observed that the p_H of each solution mixture (*i*) continuously goes on decreasing for some time after which the p_H becomes constant and, evidently, a few hours are required for the equilibrium to be attained. The reading for each solution was repeated in duplicate in all cases, and in many cases in triplicate, using each time a solution mixture independently prepared from the same stock solutions, or sometimes from different stock solutions, and in all cases the readings agreed within $\pm$ 0.01 p_H unit.

* This was done since $\log f_1$ and $\log f_2$ are linearly related to $\sqrt{\mu}$ and 'f_1' and 'f_2' both become equal to unity when $\sqrt{\mu} = 0$ (vide equations 8a and 8b).

TABLE I

Concentration of parent solutions.

Solution mixtures in c.c..			$M/10$; $C=0.1$; $\dot{p}=1$. Temp. $=34°$.		$M/5$; $C=0.2$; $\dot{p}=1$. Temp. $=32°$.		$M/3$; $C=0.333$; $\dot{p}=1$. Temp. $=32°$.	
HAc.	$Pb(NO_3)_2$.	Water.	p_H.	Increase in $[H^+]$ $(Y\times10^4)$.	p_H.	Increase in $[H^+]$ $(Y\times10^4)$.	p_H.	Increase in $[H^+]$ $(Y\times10^4)$.
x.								
1	9	...	2.73		2.43		2.22	
1	...	9	3.40	13.0	3.23	28.9	3.12	48.7
...	9	1	3.80		3.62		3.40	
2	8	...	2.60		2.30		2.12	
2	...	8	3.20	18.1	3.05	39.0	2.95	59.9
...	8	2	4.15		3.65		3.32	
3	7	...	2.55		2.25		2.07	
3	...	7	3.10	19.6	2.96	43.9	2.89	67.4
...	7	3	4.15		3.88		3.32	
4	6	...	2.50		2.23		2.00	
4	...	6	3.05	21.8	2.91	46.1	2.83	81.7
...	6	4	4.03		3.90		3.45	
4.5	5.5	...	...		2.22		1.99	
4.5	...	5.5	....	...	2.93	47.5	2.82	84.0
...	5.5	4.5	...		4.00		3.50	
5	5	...	2.48		2.20		1.98	
5	...	5	3.00	22.7	2.91	50.0	2.80	86.5
...	5	5	4.35		4.10		3.63	
5.5	4.5	...	...		2.20		1.98	
5.5	...	4.5	...	...	2.90	49.6	2 78	86.1
...	4.5	5.5	...		4.07		3.79	
6	4	...	2.49		2.21		1.99	
6	...	4	2.95	20.7	2.88	47.8	2.74	82.7
...	4	6	4.32		4.16		3.84	
6.5	3.5	...	...		2.22		2.00	
6.5	...	3.5	...	...	2.78	43.2	2.73	80.1
...	3.5	6.5	...		4.27		3.90	
7	3	...	2.50		2.22		2.02	
7	...	3	2.90	18.6	2.75	42.1	2.71	74.9
...	3	7	4.45		4.44		3.97	
7.5	2.5	...	...		2.25		2.03	
7.5	...	2.5	...	...	2.73	37.2	2.71	73.1
...	2.5	7.5	...		4.45		4.14	
8	2	...	2.53		2.27		2.13	
8	...	2	2.85	15.3	2.71	33.9	2.66	51.7
...	2	8	5.10		4.57		4.30	
9	1	...	2.60		2.35		2.15	
9	...	1	2.85	10.9	2.69	24.2	2.64	46.9
...	1	9	5.05		4.90		4.70	

The results of the p_H measurements are tabulated in Table I. The values of 'Y' have been plotted against the corresponding values of 'x' in Fig. 1. Curves I, II and III refer to $C=0.1$, 0.2 and 0.333 respectively for both parent solutions.

FIG. 1

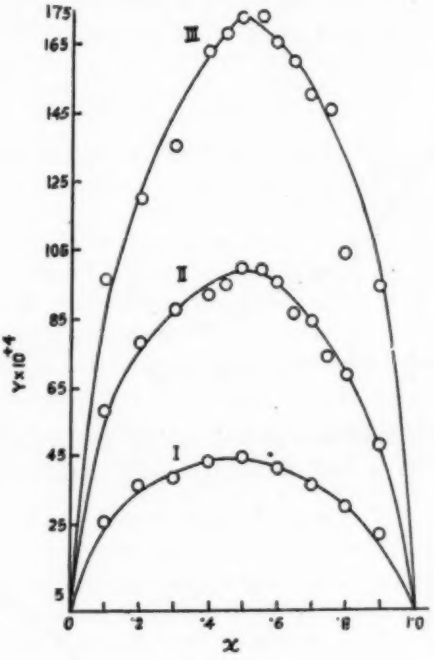


TABLE II

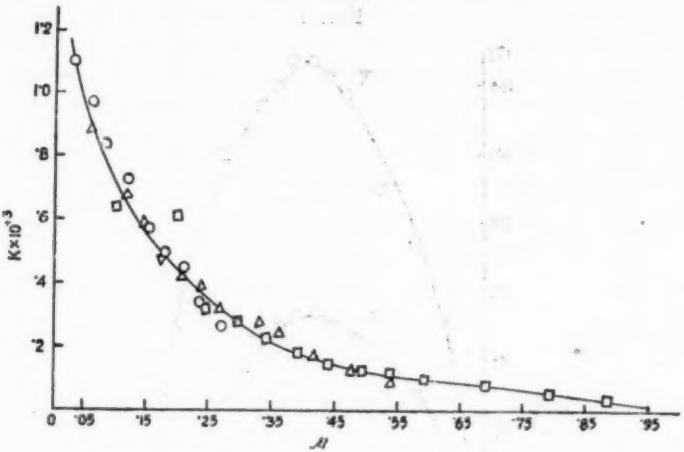
Solution mixtures in c.c.			Concentration of parent solutions.					
x.	HAc	$Pb(NO_3)_2$	$M/10$; $C=0.1$; $p=1$. Temp $=34°$.		$M/5$; $C=0.2$; $p=1$. Temp $=32°$.		$M/3$; $C=0.333$; $p=1$. Temp $=32°$.	
			μ.	$K\times10^3$.	μ.	$K\times10^3$.	μ.	$K\times10^3$.
0.10	1.0	9.0	0.2682	0.260	0.5364	0.085	0.8923	0.024*
0.20	2.0	8.0	0.2377	0.346	0.4752	0.119	0.7919	0.048
0.30	3.0	7.0	0.2075	0.450	0.4147	0.170	0.6912	0.080
0.40	4.0	6.0	0.1772	0.496	0.3545	0.236	0.5898	0.092
0.45	4.5	5.5	...	...	0.3244	2.266	0.5398	0.108
0.50	5.0	5.0	0.1472	0.573	0.2942	0.278	0.4895	0.125
0.55	5.5	4.5	...	...	0.2642	0.310	0.4398	0.148
0.60	6.0	4.0	0.1174	0.720	0.2344	0.378	0.3900	0.184
0.65	6.5	3.5	...	...	0.2047	0.416	0.3405	0.223
0.70	7.0	3.0	0.0876	0.840	0.1747	0.477	0.2909	0.282
0.75	7.5	2.5	...	...	0.1453	0.592	0.2415	0.329
0.80	8.0	2.0	0.0580	0.972	0.1156	0.673	0.1936	0.614
0.90	9.0	1.0	0.0287	1.1.3	0.0569	0.879	0.0943	0.642

N.B. The ionisation constant of acetic acid (HAc) at the temperature of the experiment (32°–40°) has been taken to be $K_a=1.75\times10^{-5}$ ("The Physical Chemistry of Electrolytic Solutions" by Harned and Owen, Ed. II, p. 580.

* Not shown in Fig. 3, but it will fall on the same straight line.

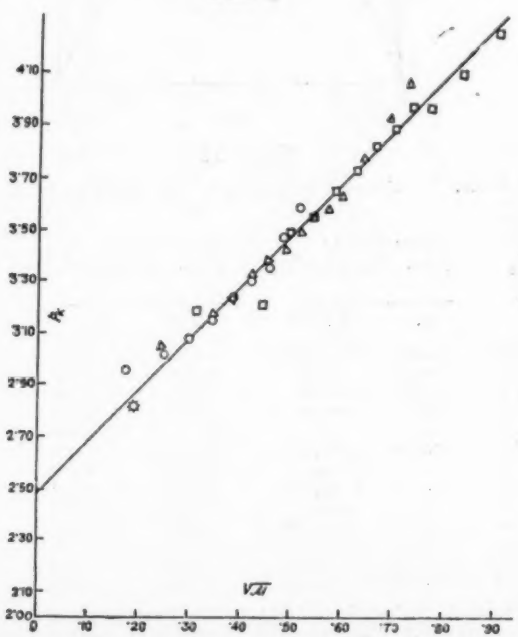
The values of 'μ' and 'K' (vide equs. 7 and 1a respectively) obtained by following different stages of calculation, as shown before, are shown in Table II. The values

FIG. 2



of 'K' obtained in Table II have been plotted against the corresponding values of the ionic strength 'μ' in Fig. 2 and, as stated already, all the points have been found to

FIG. 3



The sign ⁺ represents the plot pK against $\sqrt{\mu}$ (mean) from Part III.

lie on the same smooth curve, proving definitely the dependence of the values of 'K', calculated by the above method, on the respective ionic strength. In Fig. 3 the values of $pK = (-\log K)$ have been plotted against the corresponding values of $\sqrt{\mu}$ from Table II, and it can be seen that all the points lie on the same straight line ; this when extrapolated to $\sqrt{\mu} = 0$, gives the value of pK representing the negative exponent of the true thermodynamic constant 'K'. This value is $pK = 2.48$ and hence, $K = 3.31 \times 10^{-3}$ at 32°–34°.

Discussion

From the review of the work done in the past fifty years on the complexes formed between lead and acetate ions, summarised by Purkayastha and Sen Sarma (this *Journal*, *loc. cit.*), it is clear that the most stable complex formed in solution by mixing lead and acetate ions is $[PbAc]^+$; the higher acetate complexes are not formed in significant amounts when the acetate ion concentration is small. The study of lead nitrate and acetic acid mixtures by Job's method in the present work also corroborates this view. Considerable difference in opinion, however, exists as regards the value of the dissociation constant, 'K', for the complex $[PbAc]^+$. Edmonds and Birnbaum (*J. Amer. Chem. Soc.*, 1940, **62**, 2367) from a study of the solubility of lead iodate in solutions containing varying amounts of acetate ion at constant ionic strength, adjusted by adding appropriate amounts of ammonium perchlorate, concluded that $K = 9.65 \times 10^{-3}$ at 25° for $[PbAc]^+$ (mean value worked out from several values given). Though this value represents approximately thermodynamic constant, 'K', at the particular ionic strength employed, it is not certainly the true value for 'K' since the activity coefficients for the ions at the ionic strength employed are much less than unity and so they do not cancel out. Moreover, Purkayastha and Sen Sarma (*loc. cit.*) have pointed out that the conclusion of Edmonds and Birnbaum are based on certain arbitrary assumptions, not often justifiable.

Purkayastha and Sen Sarma (*loc. cit.*) from a study of the conductivities of solution mixtures of lead nitrate and ammonium acetate by Job's method of continued variation concluded that the dissociation constant 'K' for $[PbAc]^+$ was 40.76×10^{-3} at 30°. This work too, is open to the following objections.

(*a*). Job's method cannot yield an accurate value of 'K' for reasons already stated. However, the composition of the complex determined by this method is fairly reliable.

(*b*). The specific conductivity is not strictly an additive molecular property, since the specific conductivity of the mixture would be definitely lower than the sum of the specific conductivities of the individual parent solutions at the same dilutions, even if there is no reaction between the two, as the ionic strength of the mixture is greater.

(*c*). The value of 'K' obtained by Job's method is not the thermodynamic one in cases where the reactants and resultants are ions.

Das, Aditya and Prasad (this *Journal*, 1952, **29**, 169) from an E. M. F. study of the cell,

$$Hg_x\ Pb_y \mid \underset{C}{Pb(NO_3)_2} \parallel NH_4NO_3 \parallel \underset{C}{PbAc_2} \mid Pb_y\ Hg_x$$

have found out the thermodynamic dissociation constant of the ion $[PbAc]^+$ as 3.1×10^{-3}, assuming complete dissociation of stage (I) of the following scheme of dissociation of lead acetate in aqueous solution,

$$PbAc_2 \rightleftharpoons [PbAc]^+ + Ac^- \quad \ldots \quad \ldots \quad \text{(Stage I)}$$

$$[PbAc]^+ \rightleftharpoons Pb^{2+} + Ac^- \quad \ldots \quad \ldots \quad \ldots \quad \text{(Stage II)}$$

In a later communication Aditya and Prasad (*ibid.*, 1953, **30**, 213) from a study of the E.M.F. of cells of the type,

$$Hg \mid Hg_2Ac_2,\ PbAc_2\ (C) \parallel NH_4NO_3 \parallel NaAc,\ Hg_2Ac_2 \mid Hg$$

$$HAc\ (C_1) \qquad Solution \qquad (2C) \qquad HAc\ (C_1)$$

came to the conclusion that the first stage dissociation of lead acetate was substantially incomplete, and combining the E.M.F. data of both types of cells, they calculated the thermodynamic constant 'K_1' and 'K_2' for the first and second stages of dissociation respectively shown above ; the values of 'K_1' and 'K_2' were 30×10^{-3} and 3.7×10^{-3} respectively.

The value of 'K' given by Aditya and Prasad ($K = 3.7 \times 10^{-3}$ at 30°) (*loc. cit.*), however, appears to be the most satisfactory and agrees well with the value ($K = 3.31 \times 10^{-3}$ at 32.0-34.0°) obtained in the present work by an independent method, free from practically all the objections raised in the previous cases. The only approximation made is the neglect of the formation of polyacetato plumbites. The possibility of formation of higher acetato plumbites, e.g. $PbAc_n$ ($n = 2,3,4$ etc), in the system "lead nitrate - acetic acid - water" is however small, since $[Ac^-]$ in such a system is very low, the dissociation of acetic acid in water being very poor. Moreover, the presence of preponderating amounts of the complex $PbAc^+$ in preference to higher acetato plumbites, is amply demonstrated by the value of $m/n = 1$, obtained by the present work and by Purkayastha and Sen Sarma (*loc. cit.*) using Job's method of continued variation. Purkayastha and Sen Sarma have used ammonium acetate solution in which $[Ac^-]$ is very large, and there is a greater possibility of formation of higher acetato plumbites than in the present work, and if acetato plumbites are formed to any appreciable extent, the value of 'K' determined by Purkayastha and Sen Sarma would be more erroneous, for then, Job's formula in the form used by the authors would not have been applicable.

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART II. LEAD MONO-PROPIONATO AND MONO-FORMATO COMPLEXES

By S. K. Siddhanta and S. N. Banerjee

The composition of the complex formed between Pb^{2+} and propionate ions has been found to be $(PbProp.)^+$ from a study of the equilibrium hydrogen-ion concentrations in mixtures of equimolecular lead nitrate and propionic acid solutions by "Job's method of continued variation", using the increase of hydrogen-ion concentration as a new index. Proceeding similarly, the composition of the complex formed between Pb^{2+} and formate ions has been found to be $(PbFor)^+$.

The thermodynamic dissociation constant, K, for the equilibrium $PbProp.^+ \rightleftharpoons Pb^{2+} + Prop.^-$ has been found out as 4.57×10^{-3} at 28–30° by the direct application of "law of mass action", taking into account the activity coefficients of the individual ions, calculated from the ionic strength of the solution mixture of lead nitrate and propionic acid, employing the "Debye-Hückel limiting law". Proceeding similarly, the thermodynamic dissociation constant K for the equilibrium $(PbFor)^+ \rightleftharpoons Pb^{2+} + For.^-$ has been found to be 182.0×10^{-3} at 26–30°. The first step of dissociation of lead formate in aqueous solution, viz. $Pb(For.)_2 \rightleftharpoons (PbFor.)^+ + For.^-$ has been suggested as nearly complete, and the reasons have been advanced.

Following the same procedure adopted for lead acetato complex, described in Part I of this series (this *issue*, p. 269) the thermodynamic dissociation constants for the equilibria, $(Pb\,Prop.)^+ \rightleftharpoons Pb^{2+} + Prop.^-$ and $(PbFor.)^+ \rightleftharpoons Pb^{2+} + For.^-$,

$$K = \frac{a_{Pb^{2+}}\, a_{Prop.^-}}{a_{PbProp.^+}} = \frac{c_{Pb^{2+}}\, c_{Prop.^-}}{c_{PbProp.^+}} \cdot \frac{f_{Pb^{2+}}\, f_{Prop.^-}}{f_{PbProp.^+}} \quad \ldots \quad \ldots \quad (1)$$

$$K = \frac{a_{Pb^{2+}}\, a_{For.^-}}{a_{PbFor.^+}} = \frac{c_{Pb^{2+}}\, c_{For.^-}}{c_{PbFor.^+}} \cdot \frac{f_{Pb^{2+}}\, f_{For.^-}}{f_{PbFor.^+}} \quad \ldots \quad \ldots \quad (2)$$

(where $Prop.^-$ stands for $C_2H_5COO^-$ and $For.^-$ stands for $HCOO^-$)

have been found out from the determination of p_H of solution mixtures containing a volume '$1-x$' of lead nitrate and 'x' of propionic acid or formic acid, x varying between 0.1 and 0.9, and both parent solutions being at the same concentration, 'C'. The composition of the complex formed has been determined as in the case of lead acetato complex in Part I (*loc. cit.*) by the application of "Job's method of continued variation" using the increase, 'Y', of the hydrogen-ion concentration in the mixture, over the sum of hydrogen-ion concentrations of the parent solutions, at the same dilution, as the index property*. From the curves representing $Y-x$ plots, it has been found that the maximum value of 'Y' corresponds to the reacting proportion 1 : 1 for lead nitrate and propionic acid or formic acid. This shows that under the condition of the experiment, the following equilibrium alone is most prominent, and the formation of higher complexes, e.g. $PbProp._2$, $PbProp._3^-$ etc.

* In the present case, however, the hydrogen-ion concentration of the mixture of '$1-x$' c.c. of lead nitrate solution at concentration 'C' with 'x' c.c. of water is very small, and has therefore been neglected in calculating the value of 'Y'.

or $PbFor._2$, $PbFor_3^-$ etc. as the case may be, is negligible. The reaction can therefore be written in the case of propionic acid as

$$Pb^{2+} + HProp. \rightleftharpoons (PbProp.)^+ + H^+$$

or, in the case of formic acid as

$$Pb^{2+} + HFor. \rightleftharpoons (PbFor.)^+ + H^+,$$

assuming complete dissociation of lead nitrate and nitric acid.

EXPERIMENTAL

The lead nitrate used was of the reagent quality (E. Merck, Darmstadt) and propionic acid (B.D.H., Lab. reagent) was distilled under atmospheric pressure with anhydrous calcium chloride, and the fraction coming exactly at 141° was employed. The formic acid used was of Analar quality. All solutions were prepared with conductivity water.

Preparation of stock solutions of lead nitrate and propionic acid/formic acid, both of concentration 'C', was made exactly like lead acetato complex in Part I (vide Experimental). After keeping the mixtures as shown in Tables I and III, in a closed room for 3 hours in the case of propionic acid mixtures and 4 hours in the case of formic acid mixtures, the p_H values were determined from E.M.F. (E) measurement, using the formula noted below, at room temperature ($t°$) with the help of a Leeds and Northrup K_2-type potentiometer, using saturated calomel and quinhydrone electrodes, bridged by a saturated KCl solution (Kohlthoff and Laitinen, "p_H and Electro-titration", 2nd ed., p. 92, John Wiley).

$$p_H = \frac{0.4552 - 0.00009\,(t-25) - E}{0.0591 + 0.0002\,(t-25)}$$

The E.M.F. reading for each solution was repeated in duplicate in all cases, and in many cases in triplicate, using each time a solution mixture independently prepared from the same stock solutions, and sometimes from different stock solutions, and in all cases, the readings gave p_H values agreeing within ±0.01 unit.

FIG. 1

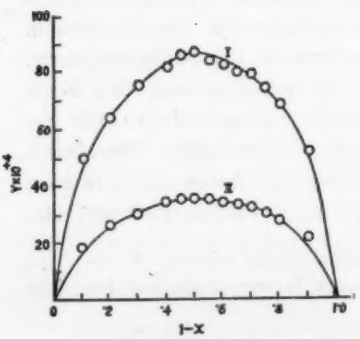

FIG. 3

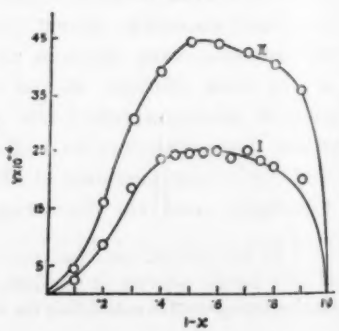

TABLE I

(HProp. stands for propionic acid)

$1-x$.	Solution mixtures in c.c.			Concentration of parent solutions			
				$M/2$; $C=0.5$; $\bar{p}=1$; Temp.$=30°$.		$M/5$; $C=0.2$; $\bar{p}=1$; Temp.$=28°$.	
	HProp.	$Pb(NO_3)_2$.	Water.	p_H.	Increase in $[H^+]$ ($Y\times10^4$).	p_H.	Increase in $[H^+]$ ($Y\times10^4$).
	9	1	...	2.14	49.53	2.486	18.4
0.1	9	...	1	2.64		2.838	
	8	2	...	2.07	63.73	2.402	26.14
0.2	8	...	2	2.67		2.87	
	7	3	...	2.02	75.55	2.37	30.07
0.3	7	...	3	2.70		2.90	
	6	4	...	2.00	81.38	2.343	33.01
0.4	6	...	4	2.73		2.94	
	5.5	4.5	...	1.985	85.92	2.335	35.15
0.45	5.5	...	4.5	2.755		2.955	
	5	5	...	1.985	86.90	2.335	35.52
0.50	5	...	5	2.78		2.97	
	4.5	5.5	...	2.00	84.15	2.343	35.30
0.55	4.5	...	5.5	2.80		2.996	
	4	6	...	2.01	82.76	2.36	34.14
0.60	4	...	6	2.825		3.022	
	3.5	6.5	...	2.027	80.17	2.377	33.17
0.65	3.5	...	6.5	2.86		3.055	
	3	7	...	2.035	79.38	2.394	32 31
0.70	3	...	7	2.89		3.094	
	2.5	7.5	...	2.065	74.62	2.424	30.12
0.75	2.5	...	7.5	2.94		3.122	
	2	8	...	2.107	68.61	2.466	27.59
0.80	2	...	8.0	3.02		3.18	
	1	9	...	2.235	51.53	2.586	21.47
0.90	1	...	9	3.173		3.35	

TABLE II

(The symbol used in the table headings and their evaluations are same as in Part I of the series *loc. cit.*).

$1-x$.	Solution mixtures in c.c.		Concentration of parent solutions.			
			$M/2$; $C=0.5$; $\bar{p}=1$; Temp.$=30°$.		$M/5$; $C=0.2$; $\bar{p}=1$; Temp.$=28°$.	
	HProp.	$Pb(NO_3)_2$.	μ.	$K\times10^3$.	μ.	$K\times10^3$.
0.1	9	1	0.1444	0.83	0.0582	1.49
0.2	8	2	0.2927	0.51	0.1171	1.04
0.3	7	3	0.4414	0.28	0.1766	0.80
0.4	6	4	0.5908	0.18	0.2361	0.57
0.45	5.5	4.5	0.6653	0.13	0.2660	0.48
0.50	5	5	0.7403	0.11	0.2950	0.42
0.55	4.5	5.5	0.8156	0.095	0.3260	0.38
0.60	4	6	0.8907	0.078	0.3561	0.35
0.65	3.5	6.5	0.9662	0.065*	0.3862	0.31
0.70	3	7	1.041	0.050*	0.4163	0.27
0.75	2.5	7.5	1.117	0.042*	0.4465	0.25
0.80	2	8	1.192	0.035*	0.4769	0.22
0.90	1	9	1.344	0.020*	0.5376	0.15

N.B. The ionisation constant of propionic acid at the temperature of the experiment (28-30°) has been taken to be $K_a = 1.33\times10^{-5}$ ("The Physical Chemistry of Electrolytic Solutions" by Harned and Owen, 2nd ed., p. 580).

* These points could not be shown in Fig. 2, but they also fall on the straight line.

FIG. 2

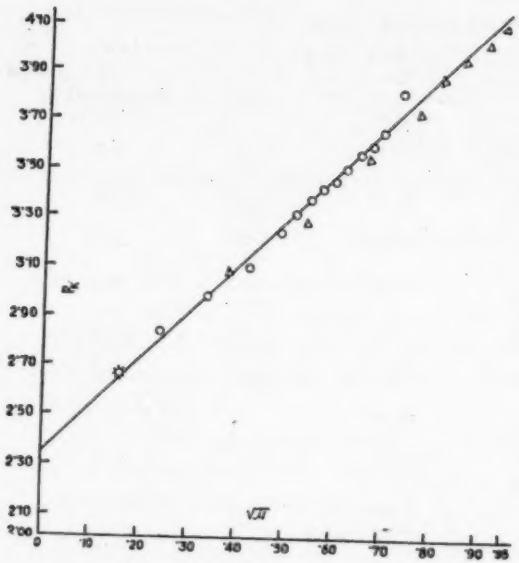

FIG. 4

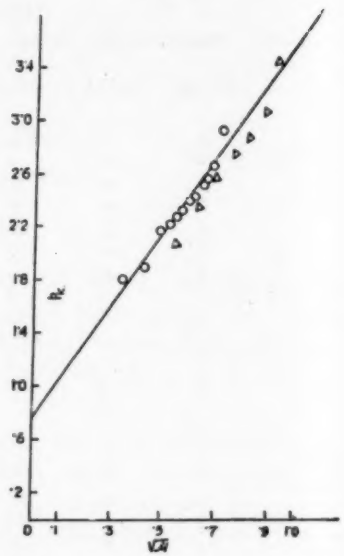

TABLE III

(HFor. stands for formic acid)

$1-x$.	Solution mixtures in c.c.			Concentration of parent solutions. $M/5$; $C=0.2$; $p=1$; Temp.$=26°$.		$M/3$; $C=0.33$; $p=1$; Temp.$=30°$.	
	HFor.	$Pb(NO_3)_2$	Water.	p_H.	Increase in (H^+) $(Y\times10^4)$.	p_H.	Increase in (H^+) $(Y\times10^4)$.
0.1	9	1	...	2.31	2.21	2 208	4 26
	9	...	1	2.33		2.239	
0.2	8	2	...	2.275	8.42	2.148	16.04
	8	...	2	2.35		2.259	
0.3	7	3	...	2.22	18.57	2.078	31.08
	7	...	3	2.38		2.280	
0.4	6	4	...	2.20	24.20	2.055	39.01
	6	...	4	2.41		2.309	
0.45	5 5	4·5	...	2.21	24.51	...	...
	5·5	...	4·5	2.43		...	...
0.50	5	5	...	2.22	24.78	2.048	44.46
	5	...	5	2 45		2 346	
0.55	4·5	5·5	...	2.236	24.97	...	...
	4·5	...	5·5	2.48		...	...
0.60	4	6.0	...	2.245	25.27	2.074	44.06
	4	...	6	2.50		2.395	
0.65	3·5	6.5	...	2.275	24.25	...	...
	3·5	...	6.5	2.54		...	...
0.70	3	7.0	...	2.286	25.46	2,111	42.46
	3	...	7	2.58		2.456	
0.75	2·5	7·5	...	2.32	23.87	...	...
	2.5	...	7·5	2.62		...	...
0.80	2	8.0	...	2.354	22.	2.169	40.47
	2	...	8	2.67		2.564	
0.90	1	9.0	...	2.464	20.01	2.259	36.11
	1	...	9	2.843		2.722	

TABLE IV

(The symbols used in the table headings and their evaluations are same as in Part I of the series, *loc. cit.*).

$1-x$.	Solution mixtures in c.c.		Concentration of parent solutions.			
			$M/5$; $C=0.2$; $p=1$; Temp. $=26°$.		$M/3$; $C=0.33$; $p=1$; Temp. $=30°$.	
	HFor.	$Pb(NO_3)_2$.	μ.	$K\times10^3$.	μ.	$K\times10^3$.
**0.10	9	1				
0.20	8	2	0.1250	15.62	0.2036	57.7*
0.30	7	3	0.1818	13.16	0.2581	8.46
0.40	6	4	0.2400	6.95	0.3948	4.38
0.45	5.5	4.5	0.2698	6.19	...	...
0.50	5.0	5.0	0.2995	5.42	0.4922	2.62
0.55	4.5	5.5	0.3293	4.89	...	...
0.60	4.0	6.0	0.3589	4.04	0.5907	1.89
0.65	3.5	6.5	0.3890	3.86	...	...
0.70	3.0	7.0	0.4185	3.02	0.6894	1.31
0.75	2.5	7.5	0.4485	2.69	...	...
0.80	2.0	8.0	0.4784	2.20	0.7883	0.84
0.90	1.0	9.0	0.5358	1.18	0.8872	0.35

N.B. The ionisation constant of formic acid at 26°-30° has been taken as $K_a=1.77\times10^{-4}$ ("The Physical Chemistry of Electrolytic Solutions" by Harned and Owen, 2nd. Ed., p. 580).

*These data could not be shown in Fig. 4.

**The values of a_{PbFor^+} for mixtures corresponding to $1-x=0.1$ for both sets of parent solutions calculated by eq. (5), Part I (*loc. cit.*), are small but negative and this indicates that $c_{PbFor^+}=0$ or negligible at the given dilution.

The results of p_H measurements for mixtures of two sets of equimolecular parent solutions of lead nitrate and propionic acid, one set having concentration $C=0.5M$ and another set $C=0.2M$, have been shown in Table I. The curves I and II in Fig. 1 represent the $Y-x$ plots from the data in Table I for $C=0.5M$ and that for $C=0.2M$ respectively. The values of 'μ' and 'K' for the solution mixtures used in this work have been obtained in the same way as described in Part I (*loc. cit.*) and these values have been shown in Table II. As in the previous case of lead acetato complex, the plot of 'K' against 'μ' obtained from Table II yields a smooth curve which has not been used to determine the value of 'K' by extrapolation. In Fig. 2 the graph pK $(=-\log K)$ against $\sqrt{\mu}$ from Table II gives a straight line curve which on extrapolation to $\sqrt{\mu}=0$ gives the value of pK corresponding to the true thermodynamic constant 'K'. These values of pK and 'K' at $\sqrt{\mu}=0$ are 2.34 and 4.57×10^{-3} at 28-30° respectively.

The results of p_H measurements for mixtures of two sets of equimolecular parent solutions of lead nitrate and formic acid, one having concentration $C=0.2$ and another set $C=0.33$, have been shown in Table III. The values of 'Y' against the corresponding values of 'x' from Table III, for mixtures of lead nitrate and formic acid solutions, both being at concentration $C=0.2M$ have been graphically represented by curve I, and those for both parent solutions at concentration $C=0.33M$ by curve II, in Fig. 3. The values of 'μ' and 'K' for the solution mixtures, studied in the present work, have been

obtained by following the same procedure as described in Part I (*loc. cit.*) of this series, and these are shown in Table IV. As in the previous case (vide Part I), the plot of 'K' against 'μ' from Table IV yields a smooth curve, which has not been used to evaluate the value of 'K' by extrapolation to zero ionic strength. In Fig. 4 the graph $pK(= -\log K)$ against $\sqrt{\mu}$ from Table IV gives a straight line curve which on extrapolation to $\sqrt{\mu}=0$ gives the value of pK corresponding to the true thermodynamic constant K. These values of pK and K at $\sqrt{\mu}=0$ are 0.74 and 182.0×10^{-3} at $26^\circ - 30^\circ$ respectively.

DISCUSSION

There appears to be no previous work on the determination of the dissociation constants of lead formate. Lead formate dissociates in two steps, viz.,

$$PbFor._2 \rightleftharpoons PbFor.^+ + For^-. \quad \ldots \quad \ldots \quad (1)$$

$$PbFor.^+ \rightleftharpoons Pb^{2+} + For.^- \quad \ldots \quad \ldots \quad (2)$$

The value of K found here is really the value of K_2, the dissociation constant for the second step. The value of K_2 is sufficiently large and the value of K_1 is expected to be even larger so that the first step dissociation may be regarded as nearly complete. The values of '$c_{PbFor.^+}$' and '$c_{Pb^{2+}}$' even in dilute solution mixtures of lead formate and nitric acid, are therefore expected to be large, so that the ionic strengths of the solution mixtures are expected to be high. Under such circumstances the Bjerrum equation for the formation function, which is essentially stoichiometric, cannot be applied with the assumption that $c_{For.^-} \approx a_{For.^-}$, in evaluating the preliminary values of k_1 and k_2, the classical mass action constants necessary for calculating the approximate ionic strengths. Also, the "Debye-Hückel limiting law" becomes inapplicable, and hence, the values of f_1 and f_2 calculated therefrom will have large errors ; moreover, in the calculation of the ionic strength, it will not be correct to make the necessary assumptions that $c_{H^+} \approx a_{H^+}$ and $c_{For^-} \approx a_{For^-}$. Hence, the value of K_1 has not been determined in case of lead formate by following the same method as in the case of "lead acetato complexes" to be discussed in Part III of this series.

Critical comments on the previous work on the complex formation between lead and propionate ions, as also on the present work will be made in Part III of this series.

The authors desire to express their best thanks to Prof. S. K. Bhattacharyya, D.Sc., F.R.I.C., F.N.I., Head of the Department of Applied Chemistry, I.I.T., for offering necessary facilities to carry out this work.

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SYNTHESIS IN ACRIDINE SERIES. PART VI. SYNTHESIS OF 5-SUBSTITUTED 1 : 2-BENZACRIDINE DERIVATIVES

By K. G. Yekundi and S. R. Patel

7-Methoxy-8-bromo-5-substituted 1:2-benzacridine and the corresponding 7-nitro derivatives have been described.

The present communication deals with the synthesis of 7-methoxy-8-bromo-5-substituted 1 : 2-benzacridine and the corresponding 7-nitro derivatives. Analogous 5-substituted 1 : 2-benzacridine derivatives with substituents like OMe in 7-position or Cl in 8-position and with other substituents in the attached 1 : 2-benzene ring have been described by Bachmann and Picha (*J. Amer. Chem. Soc.*, 1946, **68**, 1600). These compounds are similar in all respects to the corresponding simple acridine derivatives.

2 : 4-Dibromo-5-methoxybenzoic acid, obtained on bromination of *m*-methoxybenzoic acid in acetic acid solution by following the method described by Patel and Nargund (this *Journal*, 1955, **32**, 187), on condensation with α-naphthylamine gave 2-α-naphthylamino-4-bromo 5-methoxybenzoic acid in about 30% yield. The latter was cyclised to 5-chloro-7-methoxy-8-bromo-1 : 2-benzacridine (I) by heating it with phosphorus oxychloride. By the reaction of (I) with appropriate amines the corresponding 5-*N*-substituted amino-1 : 2-benzacridine derivatives were obtained. Similarly 2-α-naphthylamino-5-nitrobenzoic acid, obtained on Ullmann's condensation of 2-chloro-5-nitrobenzoic acid with α-naphthylamine, was cyclised to 5-chloro-7-nitro-1 : 2-benzacridine (II) ; starting with (II) the corresponding 5-amino-1 : 2-benzacridine derivatives were synthesised.

(I) and (II) have been characterised by preparing their 5-phenoxy derivatives (Table I).

Experimental

2-α-Naphthylamino-4-bromo-5-methoxybenzoic Acid.—A mixture of 2 : 4-dibromo-5-methoxybenzoic acid (10 g.), fused potassium carbonate (7 g.), α-naphthylamine (7 g.), amyl alcohol (40 c.c.) and a trace of copper powder was refluxed at 140-50° for 3 hours and steam-distilled. The residual solution after filtration and on acidification furnished the product as a green powder, crystallising from acetic acid in greenish yellow needles, m.p. 220-22°, yield 5 g. (Found : Equiv., 370 ; Br, 21.3. $C_{18}H_{14}O_3NBr$ requires equiv., 372; Br, 21.5%).

5-Chloro-7-methoxy-8-bromo-1 : 2-benzacridine.—The preceding acid (5 g.) was heated at 110° for about 1½ hours with $POCl_3$ (20 c.c.), excess of which was removed by diluting the cooled reaction mixture with dry petroleum ether. The petroleum ether layer was removed by decantation and the residual dark thick liquid was taken up in the required quantity of acetone. The acetone solution was poured in a thin stream in a well-stirred ammonia solution containing ice whereby the product

separated out as a fine green powder. It was collected and washed with excess of water. It crystallised from toluene in greenish yellow needles, m.p. 240°, yield 4 g. (Found: N, 3.6. $C_{18}H_{11}ONClBr$ requires N, 3.7%).

2-α-*Naphthylamino-5-nitrobenzoic acid* was obtained by condensing 2-chloro-5-nitrobenzoic acid (9 g.) with α-naphthylamine (6 g.) in a similar way as the 4-bromo-methoxy analogue. It crystallised from acetic acid in greenish yellow powder, m.p. 247-49° (decomp.), yield 4 g. Its potassium salt was sparingly soluble in hot water, from which it crystallised as yellow needles. (Found : Equiv., 309 ; N, 9.3. $C_{17}H_{12}O_4N_2$ requires equiv., 308 ; N, 9.1%).

5-*Chloro-7-nitro-*1 : 2-*benzacridine* (II) was obtained from the above acid (5 g.) by heating it with $POCl_3$ (20 c.c.) by following the method described before. It crystallised from toluene in orange needles, m.p. 252-53°, yield 3 g. (Found : Cl, 11.7. $C_{17}H_9O_2N_2Cl$ requires Cl, 11.5%).

TABLE I

(B denotes -1 : 2-benzacridine)

	Name.	Method.	Shape.	M.P.	Formula.	% N Found.	% N Calc.
1.	5-Phenoxy-7-methoxy-8-bromo-B	From (I) & phenol.	Greenish yellow powder.	172°	$C_{24}H_{16}O_2NBr$.	3.3	3.2
2.	5-Amino-7-methoxy-8-bromo-B	From (I) & $(NH_4)_2CO_3$.	Do	293-95°	$C_{18}H_{13}ON_2Br$.	7.67	7.9
3.	5-(γ-Morpholinopropyl)-amino-7-methoxy-8-bromo-B	From (I) & γ-morpholino-propyl amine.	Yellow granules	270° (decomp.)	$C_{25}H_{26}O_3N_3Br$.	8.5	8.7
4.	Dihydrochloride of (3).	...	Yellow powder	295-97° (decomp.)	$C_{25}H_{33}O_3N_3ClBr$.	7.4	7.5
5.	5-Phenoxy-7-nitro-B	From (II) & phenol.	Greenish powder	165°	$C_{23}H_{14}O_3N_2$	7.8	7.6
6.	5-Amino-7-nitro-B	From (II) & $(NH_4)_2CO_3$.	Orange powder.	298-300° (decomp.)	$C_{17}H_{11}O_3N_3$	14.9	14.5
7.	5-(δ-Diethylamino-α-methylbutyl)-amino-7-nitro-B	From (II) & δ-diethylamino-α-methylbutyl amine.	Yellow granules	228-30° (decomp.)	$C_{28}H_{33}O_3N_4Cl_3$	14.2	14.5

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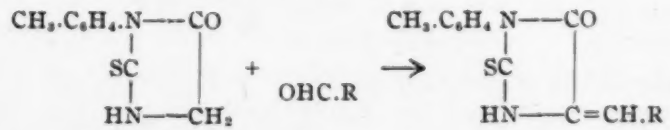
THIOHYDANTOINS AND THEIR DERIVATIVES AND USE OF SOME OF THEM IN THE ESTIMATION OF SILVER, MERCURY AND COPPER

By M. K. Rout

o-Tolylthiohydantoin and its arylidene and *N*-methylarylidene derivatives and its condensation products with nitroso compounds, ketones and quinones have been prepared. By condensation of thiohydantoin with α-naphthaldehyde and subsequent reduction with stannous chloride and hydrolysis by $(BaOH)_2$, α-naphthylalanine has been prepared The thiohydantoin has been used successfully for estimation of Ag and Hg, and dimethylaminobenzylidene-thiohydantoin for estimation of copper.

Usefulness of thiohydantoins in medicine as insecticides, resin intermediates and corrosion inhibitors is well recognised. They provide a convenient route to the synthesis of α-amino-acids, thiazole derivatives and antispasmodics. In an earlier investigation (Pujari and Rout, this *Journal*, 1954, **31**, 937) usefulness of arylidene-thiohydantoins in analytical procedures for estimation of certain metallic ions was indicated. In the present investigation, their analytical importance has been studied in detail. One of the arylidene derivatives (1-naphthylidene derivative) has also been used for the synthesis of an amino-acid, α-naphthylalanine. Preparation of quinolyl-thiohydantoins is in progress.

The thiohydantoins used for the analytical investigations are *o*- and *p* tolyl derivatives. The preparation of *p*-tolylthiohydantoin was described in a previous investigation (*loc. cit.*). *o*-Tolylthiohydantoin has been prepared in the same manner by the reaction of *o*-tolyl*iso*thiocyanate and glycine. The arylidene compounds were prepared by condensing *o*-tolylthiohydantoin with aromatic aldehydes in presence of glacial acetic acid and anhydrous sodium acetate. The reaction proceeds as follows:



These have been methylated by methyl iodide. *o*-Tolylthiohydantoin has been condensed with ketones, quinones and nitroso compounds, the condensation being carried out in presence of acetic anhydride. Preparation of one compound of each class has been illustrated in the Experimental.

For the synthesis of α-naphthylalanine, the following procedure was followed. *p*-Tolylthiohydantoin was first condensed with α-naphthaldehyde and the resulting arylidene compound was desulphurised by chloroacetic acid to yield the corresponding hydantoin. The resulting hydantoin compound was reduced by stannous chloride to the corresponding reduced hydantoin. This was converted into α-naphthylalanine by prolonged boiling with a large excess of barium hydroxide.

EXPERIMENTAL

o-Tolyl*iso*thiocyanate was prepared by the method of Dains, Brewster and Olander ("Organic Synthesis", Vol. I, p. 437). *o*-Tolylthiohydantoin was prepared by the method given in Beilstein, XXIV, Erste p. 293.

4-Benzylidene-1-o-tolyl-2-thiohydantoin.—Benzaldehyde (0.6 g.) and *o*-tolylthiohydantoin (1 g.) were refluxed in glacial acetic acid (20 c.c.) in presence of anhydrous sodium acetate (1.5 g.) for nearly 2½ hours on an wire-gauge. After heating for half an hour, the solution became clear. The reaction mixture was further heated for 2 hours. The clear brown solution was then poured into water, when a pale yellow precipitate appeared. After allowing it to stand overnight, the precipitate was filtered off and recrystallised from alcohol, m.p. 192°, yield 92%. (Found: N, 9.23; S, 11.14. $C_{17}H_{14}O_2N_2S$ requires N, 9.52; S, 10.88%).

Condensation with other aldehydes was also effected in the above manner. Their m.p. and analytical data are recorded in Table I.

TABLE I

4-Arylidene-1-o-tolyl-2-thiohydantoin.

Aldehydes taken.	M.P.	% Yield.	% Sulphur. Found.	Calc.
o-Nitrobenzaldehyde	145°	65%	9.56	9.44
m- „ „	182°	65	9.48	9.44
p- „ „	198°	75	9.37	9.44
o-Hydroxy „	175°	60	10.50	10.32
p- „ „	230°	70	10.29	10.32
Anisaldehyde	130°	85	9.82	9.88
Vanillin	186°	78	9.25	9.41
Furfuraldehyde	128°	65	11.79	11.27
Cinnamaldehyde	185°	80	10.14	10.00
p-Dimethylaminobenzaldehyde	116°	75	9.47	9.49

N-Methyl-4-benzylidene-1-o-tolylthiohydantoin.—To finely pulverised KOH (1 g.), dissolved in 95% alcohol (8 c.c.), the above compound (1 g.) was added, when a bright yellow potassium salt separated out. Methyl iodide (3 g.) was then added in small portions at a time and finally the reaction mixture was refluxed on a steam-bath for 3 to 4 hours until neutral to litmus. On cooling, the methylated thiohydantoin separated out and the inorganic salt formed was dissolved out by stirring with water. The thiohydantoin was filtered and recrystallised from alcohol, m.p. 52°, yield 85%. (Found: S, 10.12. $C_{18}H_{16}ON_2S$ requires S, 10.39%). Other arylidene derivatives were methylated in the same manner. Their m.p. and analytical data are described in Table II.

TABLE II

N-Methyl-4-arylidene-1-o-tolyl-2-thiohydantoin.

M.P.	132°	140°	154°	130°	172°	185°	167°	85°	92° (decomp.)	144°
% Yield	65	65	90	80	70	60	79	60	70	80
% Sulphur (found)	9.36	9.28	9.25	10.21	10.16	9.75	9.32	10.56	9.85	9.32
% Sulphur (calc.)	9.09	9.09	9.09	9.87	9.87	9.47	9.04	10.73	9.58	9.12

* The aldehydes taken correspond to those shown in Table I in the same order.

Condensation of o-Tolylthiohydantoin with α-Nitroso-β-naphthol.—A mixture of *o*-tolylthiohydantoin (1 g.) and α-nitroso-β-naphthol (0.8 g.) was heated under reflux in presence of acetic anhydride (15 c.c.) on a sand-bath for 1 hour. The original dark green solution finally assumed a deep brown shade. The mixture was allowed to cool and then poured into water when a brown gummy product separated out. On keeping for 24 hours, the gum hardened up and became crystalline. This was filtered off, washed with hot water, dissolved in warm dilute NaOH solution (20%) and reprecipitated on acidification with HCl (dil.) making the solution just acidic. Finally it was recrystallised from alcohol, m. p. 230°, yield 35%. (Found : S, 9.04. $C_{20}H_{12}O_2N_2S$ requires S, 8.86%).

Reaction with *p*-nitrosodimethylaniline was brought about also in the above manner, yield 36%, m.p. 174° (decomp.). (Found : S, 9.63. $C_{18}H_{18}ON_4S$ requires S, 9.47%).

Condensation with Isatin.—A mixture of *o*-tolylthiohydantoin (1.45 g.) and isatin (1 g.) was heated under reflux in presence of acetic anhydride (15 c.c.) for about 1 hour. The reaction, which was very vigorous at first, gradually subsided and it was complete when the mixture assumed a brownish yellow shade. The reaction mixture was cooled and poured into water when a precipitate came down. This was filtered, washed with hot water and finally crystallised from alcohol, m.p. 228° (decomp.), yield 82%. (Found : S, 9.44. $C_{18}H_{13}ON_3S$ requires S, 9.55%).

Condensation with anthraquinone, benzil, Michler's ketone, quinone and alizarin was effected also in the above manner. Their m.p. and analytical data are reported in Table III.

TABLE III

Condensation of o-tolylthiohydantoin with ketones or quinones.

Nature of ketones or quinones condensed.	M.P.	% Yield.	% Sulphur. Found.	Calc.
Anthraquinone	112°	60	8.16	8.08
Quinone	85°	65	9.89	9.64
Michler's ketone	135°	70	7.38	7.01
Alizarin	96°	62	6.82	6.90

α-Naphthylalanine

To accomplish its synthesis, the following intermediate compounds were prepared.

(*a*). 4-α-*Naphthylidene*-1-p-*tolylthiohydantoin*.—A mixture of *p*-tolylthiohydantoin (4 g.), 1-naphthaldehyde (3 g.), glacial acetic acid (15 to 20 c.c.) and fused sodium acetate (4 to 5 g.) was heated in an oil-bath at 140°. A clear solution was obtained at first. After 1 hour's heating, the condensation product began to separate from the hot sotution. The heating was continued for 3 to 4 hours. The reaction mixture was mixed with water, cooled and filtered. The compound was purified by recrystallisation from alcohol, m.p. 156°, yield 70%. (Found : S, 9.12. $C_{21}H_{16}ON_2S$ requires S, 9.3%).

(*b*). 4-α-*Naphthylidene*-1-p-*tolylhydantoin*.— The corresponding thiohydantoin (5 g.), prepared as above, was digested with chloroacetic acid (13 g.) in about 30 c.c. of water for 6 hours in an oil-bath at 130-40°. On concentrating to half of its bulk and cooling and filtering, the product was isolated, m.p. 180°, yield 80%. (Found : N, 8.25. $C_{21}H_{16}O_2N_2$ requires N, 8.54%).

(*c*). *Hydantoin of* α-*Naphthylalanine*.—For reduction of the preceding hydantoin, the following reaction mixture was prepared : 5 g. of hydantoin, 12.5 g. of $SnCl_2.2H_2O$, 50 c.c. of alcohol and 75 c.c. of 20% HCl. The mixture was heated on a boiling water-bath for about 2 hours and the excess of alcohol was evaporated off. The residue left behind was triturated with water, filtered and the insoluble precipitate was treated as described below. The aqueous filtrate was saturated with H_2S to precipitate tin as sulphide. After filtering off this sulphide precipitate and evaporating the filtrate to dryness, no organic residue was left.

The insoluble precipitate was proved to be the desired reduction product, m.p. 180°, yield 75%. (Found : N, 8.31. $C_{21}H_{18}O_2N_2$ requires N, 8.43 %).

(*d*). *Hydrolysis of the Reduced Hydantoin to* α-*Naphthylalanine*.—This was found to be very resistant to hydrolysis. The pure reduced hydantoin (3 g.) was suspended in about 500 c.c. of hot saturated solution of barium hydroxide and the mixture boiled under reflux till the evolution of NH_3 had ceased. This actually required digestion over a period of 40 to 50 hours. The barium was then precipitated as barium sulphate by adding the requisite amount of sulphuric acid and bringing the solution to an exact neutral point to litmus. After filtering off barium sulphate, the clear aqueous solution was evaporated to dryness when the amino-acid was obtained, m.p. 235-40°, yield 70%. (Found : N, 6.25. $C_{13}H_{13}O_2N$ requires N, 6.51%).

Use of p-*Tolylthiohydantoin in the Estimation of Silver and Mercury*

Estimation of Mercury.—A standard solution of mercuric chloride was prepared by weight standard and was further standardised by zinc ammonium thiocyanate method.

$HgCl_2$ solution (10 c.c., containing 0.04558 g. of Hg) was taken in a beaker and about 30 c.c. of water was added to it. The reagent (0.2 g.), dissolved in

about 20 c.c. of alcohol, was added gradually with stirring. The complex formed was warmed slightly on a water-bath, kept overnight and then filtered hot on G_3 crucible. The precipitate was first washed with hot water and then with water-alcohol mixture. It was dried at 105° and finally weighed. Since the weights of the complex obtained in the different experiments varied (of course within a small margin), it was considered desirable to estimate the total content of Hg in the complex which would serve as a further check on the results. For this, the procedure was slightly modified. The precipitate was collected on Whatman No. 42 filter paper and dried. The precipitate was then transferred as much as possible from the dried filter paper into an iron crucible. The filter paper was carefully made into small pieces which were put into the iron crucible along with adhering particles and the Hg content in the total quantity of the complex placed in the iron crucible was estimated by Gold crucible method. The results so obtained were then compared with the weight of mercury taken in the form of $HgCl_2$. The results agreed within 0.5%. Theoretically the weight of the complex on the basis of the proposed structure should be 0.1391 g. The weights of the complex and the weights of mercury obtained in the different experiments are recorded in Table IV. The weight of mercury obtained in each of these experiments points to the following structural formula for the complex.

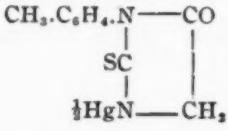


TABLE IV

Hg taken = 0.04558 g,

Wt. of the complex (g.)	...	0.1474	0.1482	0.1478	0.1486
Hg found (g.)	...	0.04533	0.04522	0.04611	0.04588
Error (g.)	...	−0.00025	−0.00036	−0.00053	+0.0003

Estimation of Silver.—A standard solution of silver nitrate was prepared by weight standard and also estimated by Mohr's method of titration using potassium chromate as indicator.

The salt solution (10 c.c. containing 0.0266 g. of $AgNO_3$) was taken in a beaker. The p_H of the solution was maintained at 3.0 by adding 50 c.c. of acetate buffer. An excess of the reagent solution (0.1 %) was added to the mixture dropwise with constant stirring till complete precipitation. The complex formed was slightly warmed on a water-bath, kept overnight and then filtered hot. The precipitate was first washed with hot water, then with 25% warm alcohol and finally with ether to free it from the reagent. The complex was dried at 120° and weighed.

Theoretically the yield of the complex on the basis of the proposed formula by taking 0.0169 g. of silver should be 0.04898 and by taking 0.04223 g. of silver, 0.1225 g. The results, which are shown in Table V, show excellent agreement with the values calculated on the basis of the proposed structure.

TABLE V

Ag. taken (g.)	...	0.0169	0.0169	0.0169	0.04223	0.04223	0.04223
Wt. of the complex (g.)	...	0.04889	0.04892	0.04882	0.1221	0.1216	0.1228
Ag found (g.)	...	0.01687	0.01688	0.01685	0.04212	0.04194	0.04236
Error (g.)	...	−0.00003	−0.00002	−0.00005	+0.00012	+0.00029	+0.00013

Ag found was calculated from the percentage of silver in the silver complex which was analysed to the formula $C_{10}H_9ON_2SAg$. (Found: N, 8.75; S, 9.95; Ag, 34.45. $C_{10}H_9ON_2S$ Ag requires N, 8.94; S, 10.23; Ag, 34.5%).

The amount of silver present in the complex was determined as follows. A definite amount of the complex was weighed in a tared porcelain crucible and heated continuously over a small flame. When the contents of the crucible became greyish white, the crucible was heated to red heat for 15 to 20 minutes. It was then cooled in a desiccator and the contents weighed. The process of ignition, cooling and weighing was repeated until a constant weight was obtained.

TABLE VI

Complex taken (g).		0.1250	0.1180	0.1456	0.2505	0.2674	0.2728
Silver found (g.)	...	0.04342	0.04172	0.05044	0.08632	0.09238	0.09409

Use of p-*Dimethylaminobenzylidene*-p-*tolylthiohydantoin in the Estimation of Copper*

A standard solution of $CuSO_4, 5H_2O$ was prepared by weight standard and was further standardised by iodometric method using starch as indicator.

Copper sulphate solution (5 c.c. containing 0.01592 g. of Cu) was taken in a beaker and about 10 c.c. of dilute ammonia and 10 c.c. of water were added to it. The solution of the reagent (0.3 g.) in 25 c.c. of rectified spirit, and 15 c.c. of acetone were then added to it with constant stirring. After stirring for 10 to 15 minutes, 5 c.c. of ammonia, 10 c.c. of water and 5 c.c. of acetone were again added, and the whole warmed for 5 minutes on a hot water-bath and then allowed to stand overnight. The complex was filtered through a previously weighed G_3 crucible and then washed with hot water. The product being somewhat soluble in warm alcohol presented some difficulties. An 1:1 cold mixture of rectified spirit and water was found by trial to be most suitable for washing. It was then dried at about 105° and weighed.

As variation in the weights of the complex, of course within a small range, was observed, it was considered necessary to estimate the content of copper in the weight of the complex obtained in each experiment. This was done as follows. The precipitate was collected on Whatman No. 42 filter paper and dried. The precipitate was transferred as much as possible from the dried filter paper into a

porcelain crucible. The filter paper was then carefully ignited into ash and was then put into the crucible along with the adhering particles. The weight of copper found in each experiment points to the proposed structure for the complex (same as in Hg complex, ½ Cu for ½ Hg). The weights of the complex and the weight of copper obtained in different experiments are recorded in Table VII.

TABLE VII

Cu taken = 0.01586 g.

Wt. of the complex (g.) ...	0.1898	0.1914	0.1926	0.1922
Cu found (g.) ...	0.01589	0.01612	0.01609	0.01597
Error (g.) ...	0.00003	0.00026	0.00023	0.00011

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SHORT NOTES

SODIUM CHLORITE AS A VOLUMETRIC REAGENT

By Ram Chand Paul and Apar Singh

Sodium chlorite is commercially available as a white finely divided crystalline material and is only slightly hygroscopic. Freshly prepared solutions are clear and colorless, but more concentrated solutions gradually turn yellow and then yellowish green if allowed to stand exposed to light. But solution of sodium chlorite, when kept in dark bottles (black painted), is quite stable for several months.

Sodium chlorite liberates iodine from potassium iodide solution in the presence of acid, and this reaction may be used for the determination of the strength of the chlorite solution. According to Bray (*Z. physikal. Chem.*, 1905, **54**, 576) for the determination of chlorite by thiosulphate titration, five minutes may be allowed for the reaction to proceed to completion before titrating in presence of acetic acid. Many other authors have proposed alternate procedures involving the use of phosphoric and sulphuric acids. Brown (*Anal. Chim. Acta*, 1952, **7**, 494) has investigated all the procedures and supports the use of sulphuric acid. He has also stressed the necessity of adding potassium iodide solution to the chlorite first, as the addition of the acid first will produce chlorine dioxide and may give rise to low results.

This reagent has been successfully used as an oxidising agent for the determination of sulphurous acid, bisulphites and sulphites by Jackson and Parson (*Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 250). The oxidation is smooth and easily controlled and is believed to proceed as

$$ClO_2^- + 4H^+ + 4e \longrightarrow Cl^- + 2H_2O.$$

In the present investigation, use has been made of the oxidising power of ICl to preoxidise various substances and of sodium chlorite to reoxidise the liberated iodine to I^+ in the presence of an excess of hydrochloric acid and potassium bromide to give the complex stable ion $(IBr_2)^-$ which is not appreciably dissociated. Lang (*Z. anal. Chem.*, 1935, **106**, 13) carried out a detailed study of the procedures involved and his modification of Andrews' titration has been used here with sodium chlorite as the oxidising agent. By this process potassium iodide, arsenious oxide, hydrazine sulphate, ferrous sulphate, potassium sulphocyanide, thallous chloride, mercurous chloride, stannous chloride, potassium ferrocyanide and hydroquinone were preoxidised with iodine monochloride and the liberated iodine was oxidised with standard sodium chlorite to the complex $(IBr_2)^-$ in the presence of a saturated solution of potassium bromide.

Sodium chlorite has also been used for the estimation of phenol and amines by using it as a bromometric reagent. Quantitative bromination method for the determination of phenol was described by Koppeschaar (*Z. anal. Chem.*, 1876, **15**, 2531). Paul and Singh (this *Journal*, 1954, **31**, 328, 605; 1955, **32**, 599, 736) have used chloramine-B and potassium metaperiodate as bromometric reagents for the estimation of various inorganic ions and organic compounds. Bromine required in the present work for bromination was obtained according to the equation,

$$ClO_2^- + 4Br^- + 4\overset{+}{H} \rightarrow \overset{-}{Cl} + 2H_2O + 2Br_2,$$

and by this method 2:4-dinitrophenol, *m*-nitrophenol, phenol, *p*-chlorophenol, anthranilic acid, *m*-nitroaniline, *p*-chloroaniline, *o*-nitroaniline and thiourea have been quantitatively estimated, following the method outlined by Paul and Singh (*loc. cit.*).

In the determination of 8-hydroxyquinoline, the modification of Fleck, Green and Ward (*Analyst*, 1934, **59**, 325) has been followed. Thus, many metals may be determined indirectly by precipitating their metallic oxinates with 8-hydroxyquinoline from their salt solutions and the organic component of the oxinate may then be determined bromometrically with sodium chlorite as usual.

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ON THE APPLICATION OF VORTMANN-FORBES REACTION TO ANTIMONY OXIDE AND THIOSULPHATE

By R. V. Iyer and J. K. Dwivedi

The reaction between antimony trioxide in alkali-lye and sodium thiosulphate was studied by Meyer (*J. Amer. Chem. Soc.*, 1922, **44**, 1498) and suggested as a clock reaction. Vortmann (*Ber.*, 1889, **22**, 2307) found the reaction between antimony trichloride and sodium thiosulphate to correspond with that of arsenious acid. Venkateswarlu (this *Journal*, 1955, **32**, 291) confirmed the existence of a minimum period of induction in the arsenious acid-sodium thiosulphate reaction in acid medium. The present work was undertaken to ascertain the existence of a similar minimum period of induction in the antimony oxide and thiosulphate reaction in presence of acids.

Procedure.—The apparatus was thoroughly cleaned with chromic acid and perfectly dried. The chemicals used were of B.D.H. sample. Sb_2O_3 was exactly weighed out for normal solution and double the amount of tartaric acid was added, followed by water. The mixture was slightly warmed to obtain a clear solution.

The tartaric acid was neutralised by the addition of sodium bicarbonate. $N/2$-Sodium thiosulphate and N-HCl were also prepared.

In a 250 c.c. conical flask Sb_2O_3 solution (25 c.c.) was taken, to which the necessary amount of water was added. In another 100 c.c. conical flask 20 c.c. of thiosulphate solution was measured out. The thiosulphate was then added to antimony oxide solution. The thiosulphate flask was washed with the requisite amount of water and added to the antimony oxide. Finally the N-HCl was added and the stop-watch started immediately. The flask was then thoroughly shaken and the time was noted when the first turbidity of antimony sulphide appeared. In each set the total volume was kept constant at 100 c.c. The results obtained are recorded in Table I.

TABLE I

Sb_2O_3 taken each time = 25 c.c.
Sodium thiosulphate taken each time = 20 c.c.

Water added.	Water for rinsing thiosulphate flask.	N-HCl and N-H_2SO_4.	Induction period for HCl.	Induction period for H_2SO_4.
25 c.c.	20 c.c.	10 c.c.	430 sec.	265 sec.
20	20	15	283	172
20	15	20	178	116
15	15	25	105	76
15	10	30	58.8	69
10	10	35	47.2	58.5
5	10	40	68	102
5	5	45	98.5	146
0	5	50	126	189

From the results it is thus clearly established that there does exist a minimum period of induction in this reaction also. Further work is in progress.

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Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
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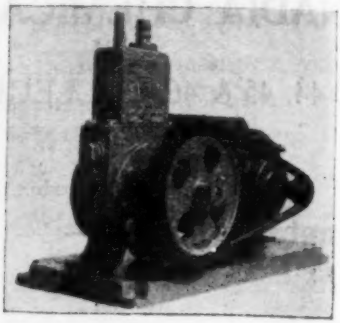

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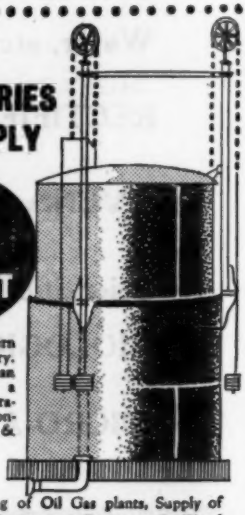

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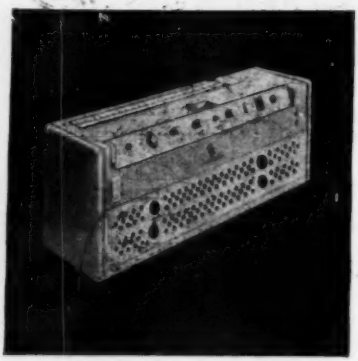

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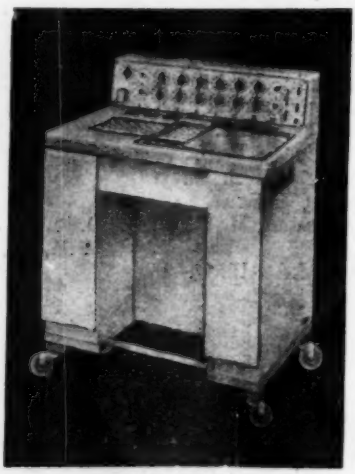

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